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SULFURIC ACID REGENERATION WASTE DISPOSAL TECHNOLOGY

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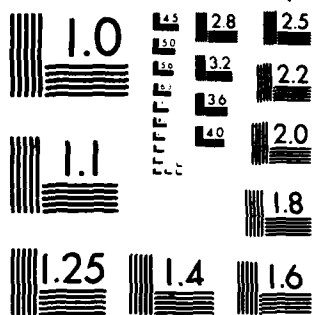
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Final Report  
United States Department of Defense  
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Washington, D.C.  
November 1986

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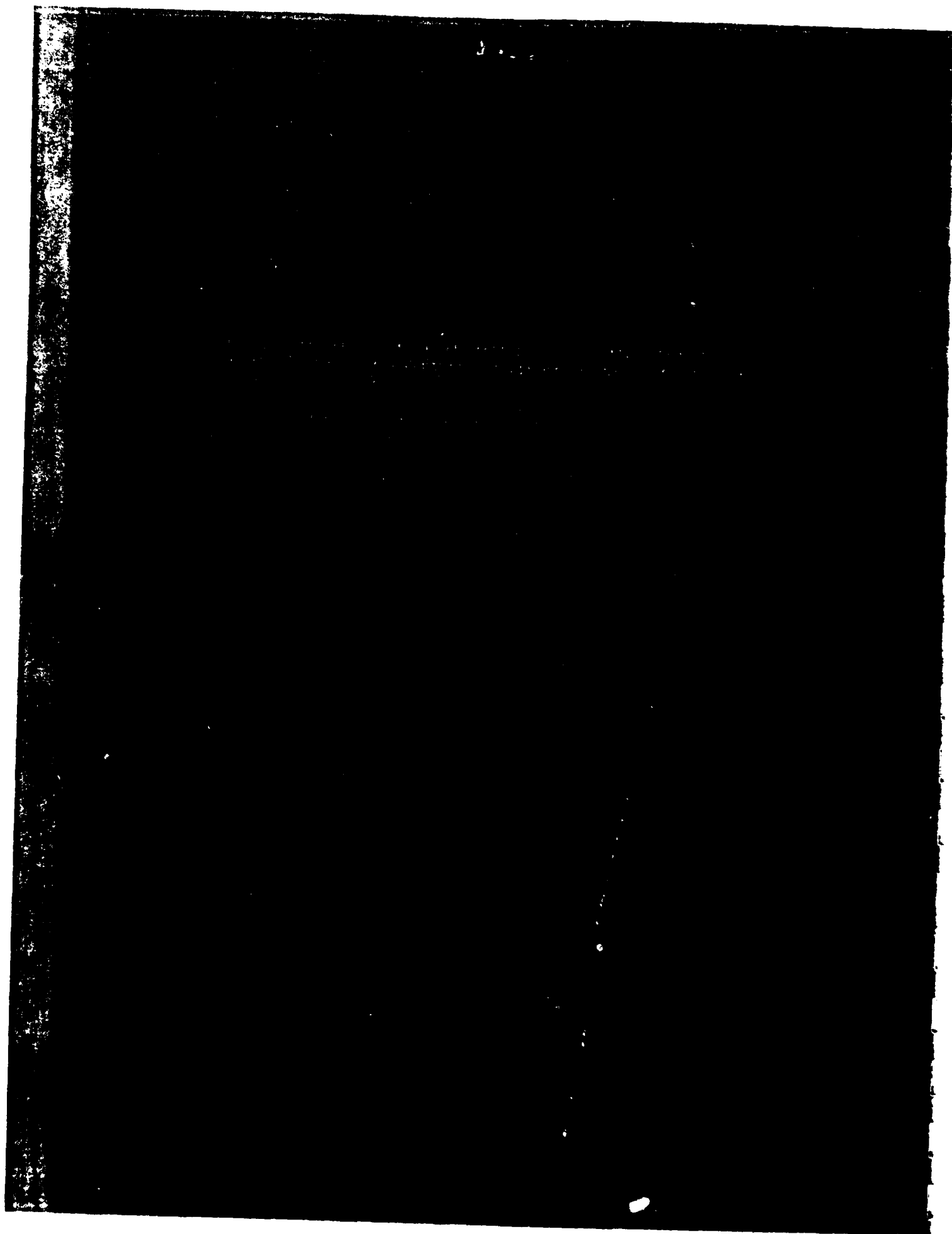
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Final Report to 12  
**United States Army**  
**Toxic and Hazardous**  
**Materials Agency**  
**November 1986**

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## **Sulfuric Acid Regeneration Waste Disposal Technology**

**(Task Order Number 2)**

### **Final Report**

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**Program Manager**

**D.E. Johnson — Task Leader**

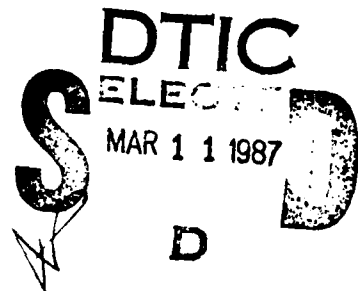
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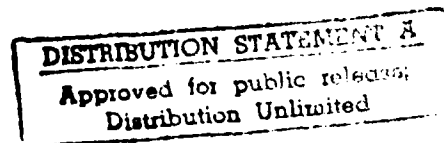
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 **Arthur D. Little, Inc.**

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Presumably because of concern at one time for soluble sulfate, two AAPs have secondary treatment: 1) ion exchange to remove the soluble calcium (Ca) and sulfate ( $\text{SO}_4$ ) ions (Volunteer AAP); and 2) barium (Ba) precipitation to remove the soluble  $\text{SO}_4$ , followed by ion exchange (Joliet AAP). Secondary treatment would permit total recycle of the process water, thus achieving zero discharge; however, we question the utility of both of these systems in achieving any improvement in the total environment of the watersheds of the plants in question.

(Keywords:)

In considering new technologies to meet potential stringent limitations such as zero discharge of pollutants, Mechanical Vapor Recompression (MVR) evaporation, for complete recycle of the sulfuric acid, was noted to have the highest environmental and process rating along with the lowest operating cost. However, it was also estimated to have the highest capital cost of any system considered, and therefore high annualized cost, except at very high operating rates. Also, there is only limited experience using centrifugal compressors in this very corrosive service.

#### Recommendations

1. The adequacy (or inadequacy) of the currently designed lime precipitation systems should be documented.
2. Obvious modifications to improve the performance of the process should be tested at an operating AAP, including the parameters of residence time, pH control, and crystal formation.
3. The efficacy of the secondary treatment systems at Volunteer and Joliet AAPs should be reviewed to see if one would ever consider operating these systems if and when the AAPs are reactivated.
4. If the Army is interested in developing an advanced zero discharge system, serious consideration should be given to testing the MVR Evaporation System for total acid and water recycle.

## EXECUTIVE SUMMARY

### Findings and Conclusions

All U.S. Army Ammunition Plants (AAPs) having sulfuric acid regeneration (SAR) facilities use lime precipitation as the principal means of acid wastewater neutralization. This is as an advanced system as is used in industrial practice. However, lime precipitation could not meet zero discharge of pollutants should these be promulgated for the sulfuric acid industry. In fact it discharges a water high in soluble sulfates. Further, based on the only current experience at Radford AAP, this process is plagued with: excessive scaling, poor pH and turbidity control, and excessive maintenance and downtime.

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## SECTION I

### INTRODUCTION

#### 1.1 Background

At U.S. Army ammunition plants (AAPs), sulfuric acid ( $H_2SO_4$ ) in excess of 100% concentration (oleum) is used as a catalyst and dehydrating agent in preparing various explosives (trinitrotoluene (TNT), nitroglycerine (NG), etc.) by nitration. In these operations, the  $H_2SO_4$  is not consumed by the chemical reactions, per se. The spent acid, roughly 70% concentration, that has been diluted by chemical water of reaction, is reconcentrated for reuse in a Sulfuric Acid Regeneration Plant (SAR). The water entering the system with the spent acid emerges from the SAR as a dilute  $H_2SO_4$  acid stream, which combined with pump seal water, etc., has a concentration of 1 to 3%  $H_2SO_4$ . While fairly dilute it is still a strong acid,  $pH < 1$ , and for an SAR producing 500 tons/day of oleum can amount to 10 to 15 tons/day of lost acid that must be neutralized before going into a receiving stream.

#### 1.2 Objective and Scope

The two objectives of this study were to:

1. Quantify and evaluate inadequacies and deficiencies in current SAR waste treatment practice; and
2. Develop a test program to achieve the necessary improved waste management technology.

The scope of work to achieve these objectives included:

- an assessment of the Radford AAP waste treatment process by plant visit and analysis of historic data;
- a review of the acid waste treatment practices of other AAPs that have SAR facilities;
- a survey of industrial acid waste treatment practices;
- ranking existing and proposed new technologies for treating SAR waste acid; and
- developing a test plan for an improved waste acid treatment process.

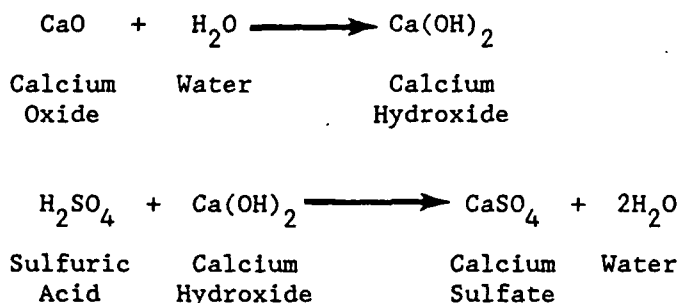
Because of a paucity of data on characteristics of SAR wastewater, the effort budgeted for analysis of the data was shifted to determining individual state standards for soluble sulfate in streams receiving AAP waste acid effluent.

## SECTION 2

### WASTE ACID NEUTRALIZATION PRACTICE

Typical SAR wastewater contaminants consist almost solely of  $H_2SO_4$  with essentially no suspended solids, nitrates, organic matter or biological oxygen demand/chemical oxygen demand (BOD/COD). The treatment of these simple, and other more complex types of acid wastes, consists of neutralization with either sodium hydroxide (NaOH), limestone ( $CaCO_3$ ), or calcium hydroxide ( $Ca(OH)_2$ ), i.e., hydrated lime.

All of the AAPs use hydrated lime as the neutralizing agent, shown by the following reactions:



The resultant calcium sulfate, or gypsum should precipitate as a fairly easily settleable white solid. One inherent problem with this process is the high solubility of calcium sulfate, about 2300 ppm. However, it should be pointed out that this process typically removes 90 to 93% of the sulfate ion from the acid stream; whereas the sodium hydroxide process merely neutralizes the sulfuric acid but removes none of the sulfate ion. Rather, all the sulfate would pass into the receiving stream as soluble sodium sulfate.

Two of the AAPs with SAR facilities have secondary or tertiary treatment to further reduce the soluble sulfate discharged. However, since lime neutralization is the main means of neutralization of the waste acid for all of the AAPs (and the only treatment for most of them), its deficiencies and potential for improvement are one of the main objectives of this study.

The Radford AAP has the only SAR, and therefore the only SAR waste treatment process, that has operated in recent years, so that it was the obvious choice for study.

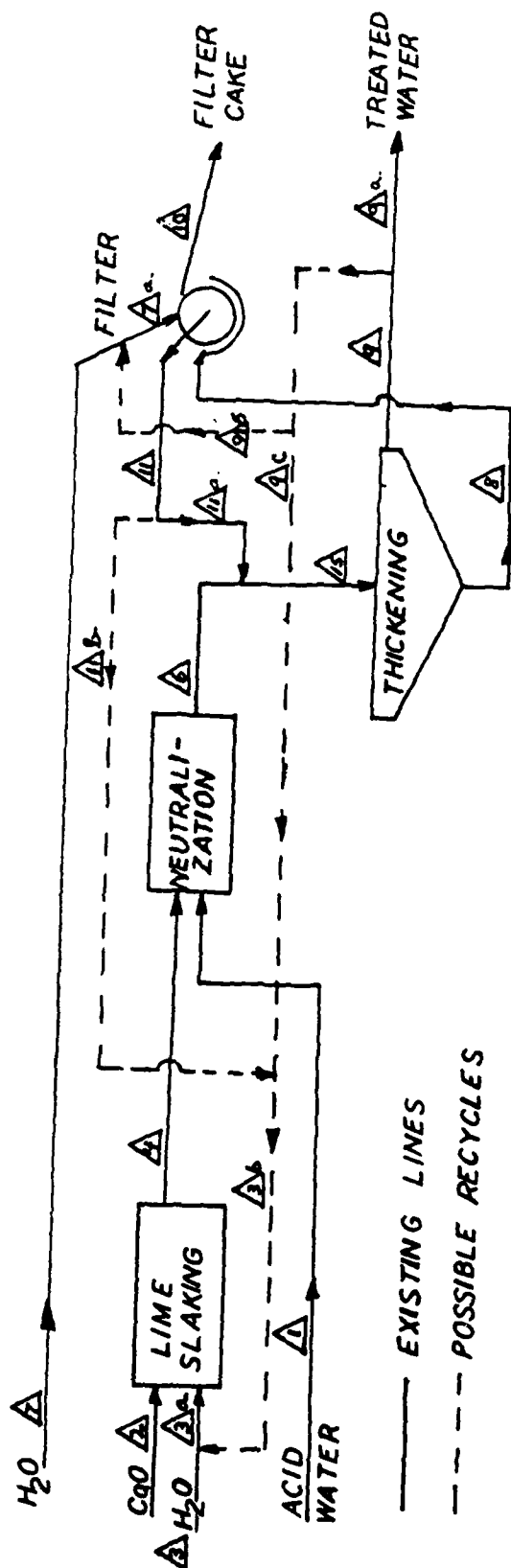
#### 2.1 Radford AAP as an Example

##### 2.1.1 Steady State Design Conditions

Figure 2-1 shows the as designed process flow schematic for the Radford AAP acid neutralization facility. At the bottom of the figure we show the design flow rates calculated from material balance considerations

FIGURE 2-1

RADFORD NEUTRALIZATION SYSTEM



ASSUMED 0.0% RE-EQUILIBRATION:									
Waste									
PROCESS LINE #	1	2	3	4	5	6	7	8	9
Water, lbs/hr	43500	0	10953	10953	0	10664	54164	15000	26564
Sulfuric Acid, %	137%	0	0	0	0	0	0	0	0
CaO	0	0	0	0	0	0	0	0	0
Calcium Hydroxide	0	0	0	0	0	0	0	0	0
Ca(OH) <sub>2</sub> , 2H <sub>2</sub> O, solid	0	0	0	0	0	0	0	0	0
Ca(OH) <sub>2</sub> , 2H <sub>2</sub> O, soluble	0	0	0	0	0	0	0	0	0
Total	43500	0	10953	10953	0	10664	54164	15000	26564
Dissolved Calcium Sulfate, ppm	0	0	0	0	0	0	0	0	0
Theor Minimum: Calc'd @ 100.0% re-equilibration:	0	0	0	0	0	0	0	0	0
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CaO	0	0	0	0	0	0	0	0	0
Calcium Hydroxide	0	0	0	0	0	0	0	0	0
Ca(OH) <sub>2</sub> , 2H <sub>2</sub> O, solid	0	0	0	0	0	0	0	0	0
Ca(OH) <sub>2</sub> , 2H <sub>2</sub> O, soluble	0	0	0	0	0	0	0	0	0
Total	43500	0	10953	10953	0	10664	54164	15000	26564
Dissolved Calcium Sulfate, ppm	0	0	0	0	0	0	0	0	0
Theor Minimum: Calc'd @ 100.0% re-equilibration:	0	0	0	0	0	0	0	0	0

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Waste									
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CaO	0	0	0	0	0	0	0	0	0
Calcium Hydroxide	0	0	0	0	0	0	0	0	0
Ca(OH) <sub>2</sub> , 2H <sub>2</sub> O, solid	0	0	0	0	0	0	0	0	0
Ca(OH) <sub>2</sub> , 2H <sub>2</sub> O, soluble	0	0	0	0	0	0	0	0	0
Total	43500	0	10953	10953	0	10664	54164	15000	26564
Dissolved Calcium Sulfate, ppm	0	0	0	0	0	0	0	0	0
Theor Minimum: Calc'd @ 100.0% re-equilibration:	0	0	0	0	0	0	0	0	0
Waste									
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Sulfuric Acid, %	137%	0	0	0	0	0	0	0	0
CaO	0	0	0	0	0	0	0	0	0
Calcium Hydroxide	0	0	0	0	0	0	0	0	0
Ca(OH) <sub>2</sub> , 2H <sub>2</sub> O, solid	0	0	0	0	0	0	0	0	0
Ca(OH) <sub>2</sub> , 2H <sub>2</sub> O, soluble	0	0	0	0	0	0	0	0	0
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Theor Minimum: Calc'd @ 100.0% re-equilibration:	0	0	0	0	0	0	0	0	0



using the Lotus "1 2 3" spread sheet. The program also calculated the theoretical dissolved  $\text{CaSO}_4$  concentration in each stream on the assumptions of zero and 100% re-equilibration of  $\text{CaSO}_4$  in the thickener and in filter washing; we have presumed that the neutralization/precipitation step always produces a saturated  $\text{CaSO}_4$  solution.

The current process flow scheme is indicated by solid lines (the dotted lines indicate potential recycle schemes). It will be noted that in addition to the dilute acid waste, fresh water is introduced into the neutralization facility for: (1) slaking of the lime; and (2) washing mother liquor from the filter cake. It can be seen from the table on the bottom of Figure 2-1 that these two fresh water streams account for 37% of the total hydraulic load. Since the total  $\text{SO}_4$  discharged to the river is the product of its solubility in the water times the hydraulic flow rate, any reduction in water flow rate will reduce the total amount of  $\text{SO}_4$  discharged, in terms of kg/day.

#### 2.1.2 Process Improvements Via Internal Water Recycle

Radford AAP personnel have proposed several schemes for recycling treated (neutralized) water to replace fresh water for the above slaking and washing operations (Ref. 44). Such possible recycles are shown in the flow chart of Figure 2-1 by dotted lines. (It should be noted that for the base case there is no recycling; all of these proposed recycles carry zero flow rate.)

Examining the tables at the bottom of Figure 2-1 shows that the treated water discharged from the thickener, if saturated, i.e., 100% re-equilibration of  $\text{CaSO}_4$  between solid and water phase in the thickener, would discharge 153 lb/hr of soluble  $\text{CaSO}_4$  at designed operating rates (45,074 lb/hr of 3.5 wt.%  $\text{H}_2\text{SO}_4$  wastewater). If the fresh water used in filter washing resulted in essentially zero re-solution of  $\text{CaSO}_4$  in the thickeners, then the discharge would have only 1693 ppm of dissolved  $\text{CaSO}_4$ , or only 115 lb/hr of soluble sulfate in the discharge. The true soluble  $\text{CaSO}_4$  discharge is obviously somewhere between these two extremes.

Figure 2-2 shows the flow rates and compositions that would prevail if treated water were used 100% in place of fresh water for the lime slaking and filter washing. Depending on percent re-equilibrium of  $\text{CaSO}_4$  in the thickeners, the discharge of soluble sulfate can be reduced to be between 90 and 95 lb/hr, i.e., 22 to 38% reduction over the classical system having no recycles.

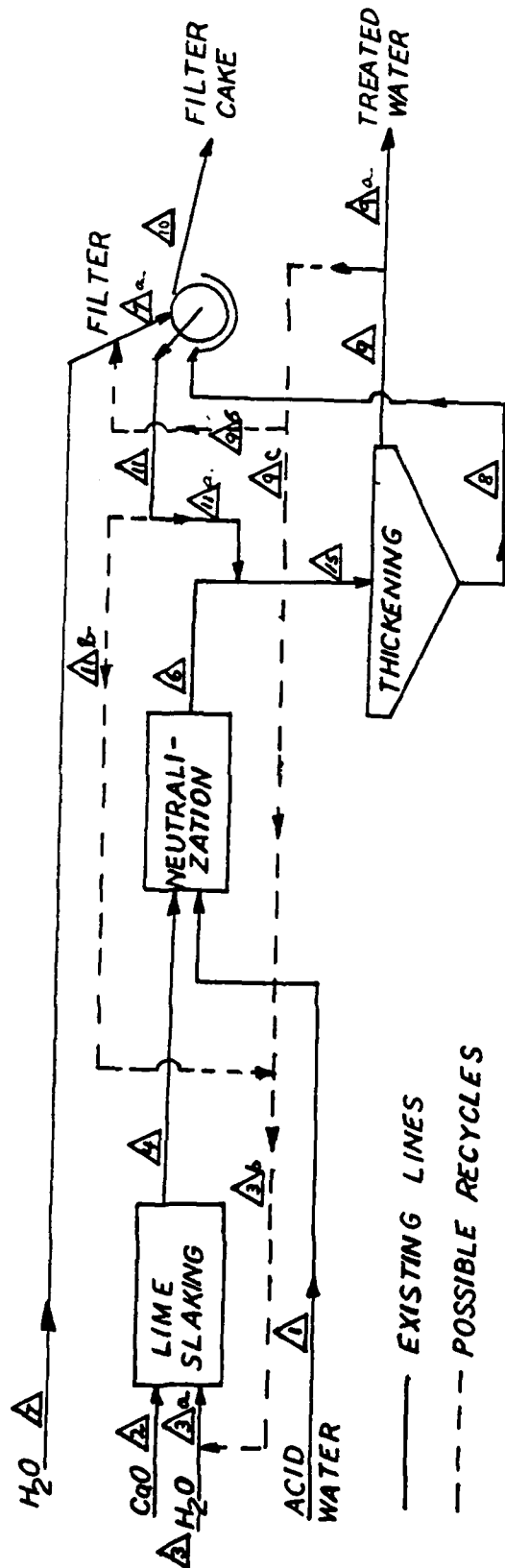
#### 2.1.3 Current Problems

Although the lime precipitation process involves only the simplest of chemistry, operation of the process is fraught with problems. These include:

- Severe scaling of equipment and sensors resulting in:
  - high maintenance costs
  - poor mechanical efficiency

FIGURE 2-2

RADFORD NEUTRALIZATION SYSTEM WITH RECYCLE



ASSUMED 0.0% RE-EQUILIBRATION:									
Waste									
PROCESS LINE #	1	2	3	3a	3b	3c	3d	3e	3f
Water, lb/hr	43500	0	0	10953	10953	10664	54164	0	0
Sulfuric Acid, lb/hr	1574	0	0	0	0	0	0	0	0
CaO	0	0	0	0	0	0	0	0	0
Calcium Hydroxide	0	0	0	0	0	0	0	0	0
Ca2SO4.2H2O, solid	0	0	0	0	0	0	0	0	0
Ca2SO4.2H2O, soluble	0	0	0	0	0	0	0	0	0
Total	45074	900	0	10976	10976	11876	56950	0	0
Dissolved Calcium Sulfate, ppm	0	0	0	0	0	0	0	0	0
Theor. Minimum	0	0	0	0	0	0	0	0	0
Calc'd @ 0.0% re-equilibration:	0	0	0	0	0	0	0	0	0

ASSUMED 100.0% RE-EQUILIBRATION:									
Waste									
PROCESS LINE #	1	2	3	3a	3b	3c	3d	3e	3f
Water, lb/hr	43500	0	0	10953	10953	10664	54164	0	0
Sulfuric Acid, lb/hr	1574	0	0	0	0	0	0	0	0
CaO	0	0	0	0	0	0	0	0	0
Calcium Hydroxide	0	0	0	0	0	0	0	0	0
Ca2SO4.2H2O, solid	0	0	0	0	0	0	0	0	0
Ca2SO4.2H2O, soluble	0	0	0	0	0	0	0	0	0
Total	45074	900	0	10976	10976	11876	56950	0	0
Dissolved Calcium Sulfate, ppm	0	0	0	0	0	0	0	0	0
Theor. Minimum	0	0	0	0	0	0	0	0	0
Calc'd @ 100.0% re-equilibration:	0	0	0	0	0	0	0	0	0

- Poor pH control due to:
  - scaling
  - slow rate of reaction
- Poor settling characteristics of finely precipitated  $\text{CaSO}_4$
- High solubility of the  $\text{CaSO}_4$  precipitate:
  - nearly 2300 ppm
- Too little sludge for proper filter operation, when treating dilute sulfuric acid waste streams (1/2% to 1%).

The final problem, too dilute acid, may be a problem of having the same quantity of acid flowing through the waste treatment plant, but being dilute, having too much water associated with it, and, therefore, residence time for reaction, settling, etc., being too short. We simply could not find data to document this hypothesis as data keeping (as required by the state and done by the plant) was very meager.

The dilute acid could result from: 1) poor operation of the SAR (leaking condenser tubes, pump glands, etc.); or 2) the relative production of TNT vs nitrocellulose (NC) and nitroglycerin (NG). Figure 2-3 shows that waste acid from TNT runs of necessity only 60% concentration as opposed to up to 93% concentration from the NC and NG processes, since the latter spent acid goes through a concentrator in the operation of separating the nitric and sulfuric acids.

#### 2.1.4 Existing Operating Data

Radford AAP was, at the time of this effort, the most active AAP, and, to our knowledge, the only one operating its SAR. (None of the other SAR Facilities have operated since 1978 or earlier.) For this reason we had to concentrate our data gathering efforts at Radford AAP, recognizing before the study started that there was very little data available on operation of the acid neutralization facility even there. Table 2-1 shows the only readily available data from Radford AAP on the outfall from the neutralization plant (before dilution with other waters upstream of Environmental Protection Agency (EPA) designated outfall 004.) This meager data, presumably daily composites for two days in March, two in July, and one in November 1982, show soluble sulfate as high as 1618 to 1958 ppm. Based on solubility of calcium sulfate at 2250 ppm, maximum  $\text{SO}_4$  ion would be only 1588 ppm. The reported March 1982 data of 1958 ppm  $\text{SO}_4$  is 23% above the theoretical solubility and may have been due to very fine precipitated  $\text{CaSO}_4$ , so fine as to pass through the 0.45 micron filter used in preparing a sample for analysis.

The only other available data on performance of the neutralization system was from the EPA designated outfall No. 004, where the SAR neutralized waters have been diluted further by a factor of about 2.5 from cooling water from steam power plant coal pile run off, etc.

Table 2-2, special data taken during operation of the SAR in November to December 1984, shows the oleum production of the SAR and the flow rate of treated waste from the acid neutralization plant. Figure 2-4 is a

FIGURE 2-3  
Generalized Flow Waste Acids  
Radford AAP

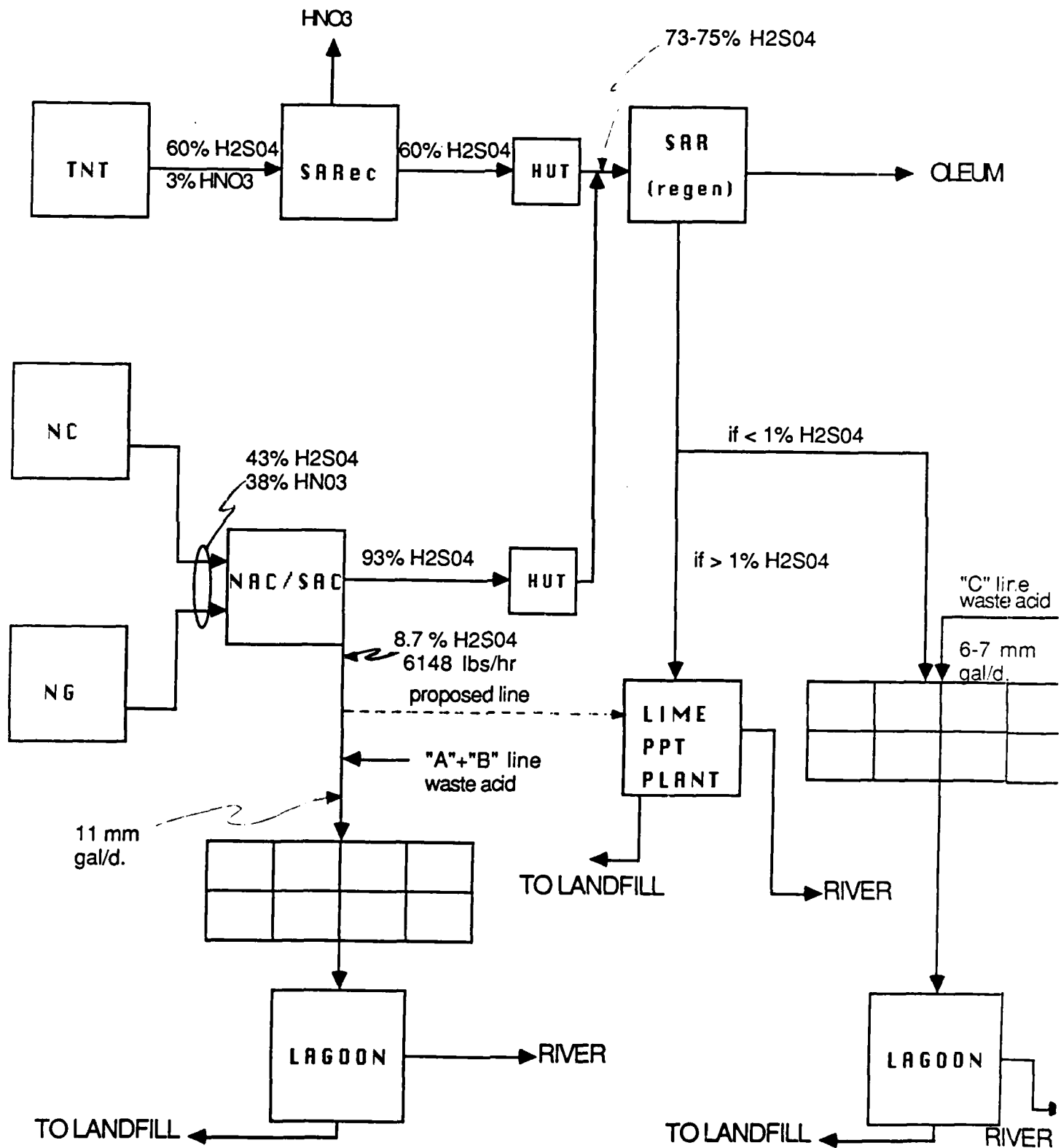


TABLE 2-1

ANALYSES OF OUTFALL 401 SAMPLES (EFFLUENT  
FROM SAR WASTEWATER TREATMENT PLANT)

<u>Month</u> <u>(1982)</u>	<u>pH</u>	<u>Total</u> <u>Suspended</u> <u>Solids, mg/L</u>	<u>Sulfates</u> <u>mg SO<sub>4</sub>/L</u>	<u>COD</u> <u>mg O<sub>2</sub>/L</u>	<u>BOD</u> <u>mg O<sub>2</sub>/L</u>
March	6.71	56	1618	22	<1
	4.83	34	1958	8	0.6
July	9.27	54	990	23	<1
	9.52	9	1090	20	1.7
November	11.50	33	292	20	1.7

Source: Hercules Aerospace Company (Radford AAP).

TABLE 2-2

APPROXIMATE AVERAGE FLOW RATES AND PH FOR EFFLUENT  
FROM SAR WASTEWATER TREATMENT PLANT (RADFORD AAP)

<u>Date</u>	<u>pH</u>	<u>Flow rate (gal/min)</u>	<u>Oleum Production (tons/day)</u>
12/17/84	9	220	506
12/16/84	9	260	429
12/15/84	9	280	471
12/14/84	8.5	240	482
12/13/84	9	240	471
12/12/84*	-	-	156
12/10/84*	-	-	114
12/9/84	8.5	260	450
12/8/84	-	260	42
12/7/84	9	280	496
12/6/84	9	260	471
12/5/84	7.5	230	178
11/23/84	7	240	186
11/22/84	8.5	230	375
11/21/84	8.5	220	464
11/20/84	8	230	475
11/19/84	8.5	200	443
11/18/84	8	160	441
11/17/84	8	160	450
11/16/84	9	152	452
11/15/84*	6	0-160	
11/13/84	9	180	144
11/12/84	11.5	160	230
11/11/84	11.5	160	276
11/10/84*	3-11 erratic	40-160 erratic	325

\*Not used in data analysis of Figure 2-4.

Source: Hercules Aerospace Company (Radford AAP).

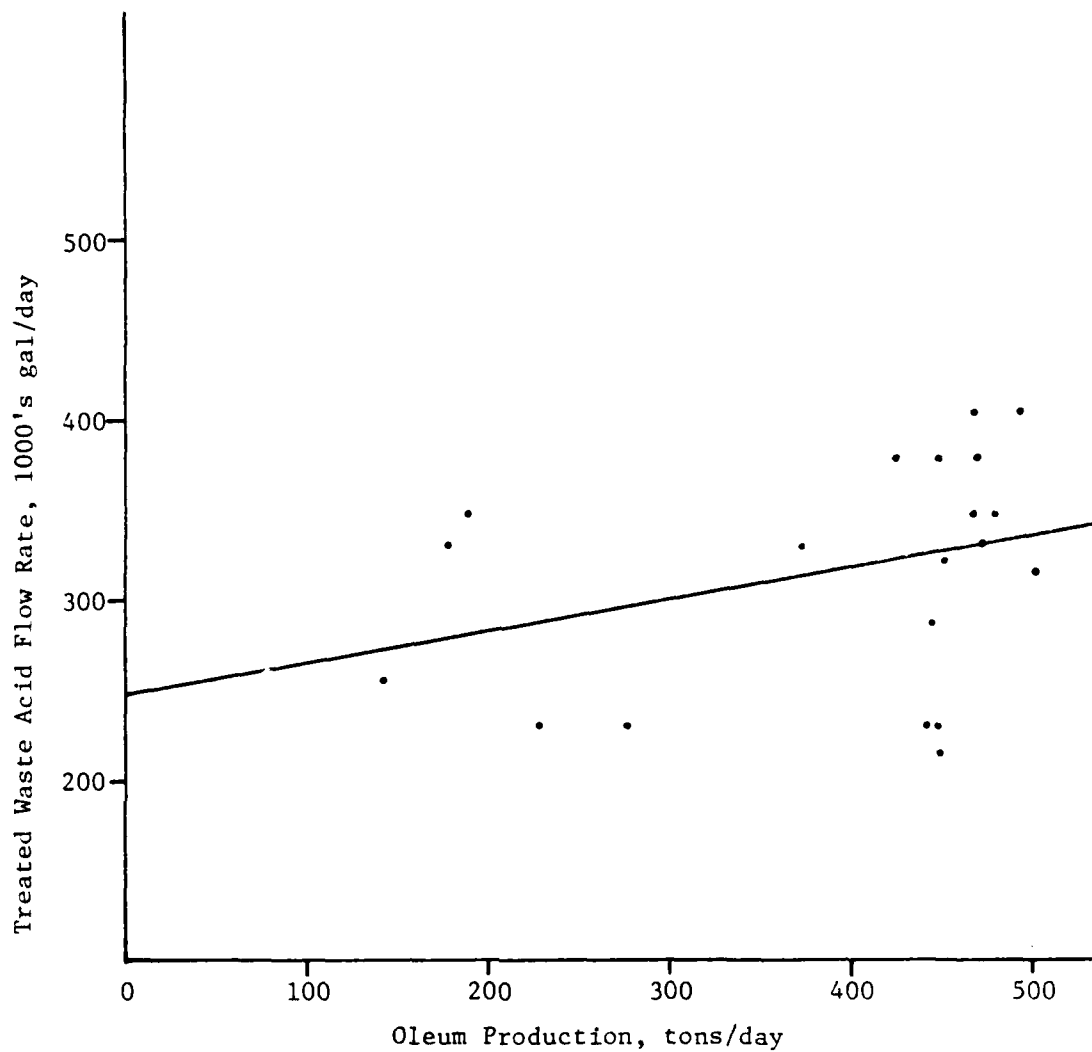


FIGURE 2-4

TREATED WASTE ACID FLOW RATE  
VS. OLEUM PRODUCTION  
(Radford AAP 11/10/84-12/17/84)

Source: Arthur D. Little, Inc.

plot of this data. It can be seen that there is very little correlation between oleum production and waste acid load (correlation coefficient  $r = .32$ ), the intercept indicating 250,000 gal/day flow rate even when the plant is not operating. Further, the low correlation coefficient suggests that only 10% of the variability in flow rate is associated with variability in oleum production rates ( $r^2 = .32^2 = .104$ ). Other AAPs have even smaller percents of their acid waters coming from their respective SAR plants so that one would expect as poor or poorer correlations of acid load with SAR production.

The National Pollutant Discharge Elimination System (NPDES) permit requires one daily 24 hour composite/week, re: 4 samples/month, with only the average and maximum values being reported. Table 2-3 shows for each month the average and maximum 24 hour composite (4 samples per month) from outfall No. 004 which as stated earlier includes the acid neutralization plant effluent.

Figure 2-5 is a plot of the total days of operation of the oleum plant within a monthly period versus the maximum reported sulfate concentration from the 004 outfall (this is only for a seven-month period, September 23, 1984, to April 20, 1985, a period where we had data on operation of the oleum plant). There is a very poor correlation as expected from the nature of the data. It is interesting to note that the maximum reported sulfate concentration, 700 ppm, corresponds to roughly a 2.25 dilution when compared to the 1558 theoretical saturation of sulfate ion, i.e., sometimes the NPDES sampling corresponded to operation of the SAR and its associated acid neutralization facilities.

Clearly, the meager data above is totally inadequate for characterizing either the dilute waste acid load from an operating SAR or the ability of a lime neutralization system to effectively respond to changing hydraulic or total acidity loads. In Section 4, we outline a proposed sampling plan to obtain the necessary data for proper analysis of an acid/lime neutralization facility.

## 2.2 Other AAPs

### 2.2.1 Summary Overview of Processes

Figure 2-6 summarizes the SAR waste acid neutralization facilities of five of the AAPs. It can be seen that all but one (Sunflower AAP) use a clarifier to concentrate the resultant  $\text{CaSO}_4$  sludge; three AAPs (Radford, Volunteer and Joliet) also vacuum filter the sludge before landfilling; and Newport AAP landfills the thickened sludge directly to a lagoon, the lagoon clarified liquor overflowing to the river.

Sunflower has the simplest system, the dilute  $\text{CaSO}_4$  slurry from their batch neutralization operation going directly to an evaporation lagoon, where, theoretically, natural evaporation exceeds the rainfall of the area.

As indicated in Figure 2-6, two AAPs, Volunteer and Joliet, have ion exchange and barium precipitation/ion exchange, respectively, for further reducing the soluble sulfate in the clarified effluent. These



TABLE 2-3  
RADFORD AAP  
SUSPEND SOLIDS AND SULFATES - DISCHARGE 004

<u>Date</u>	<u>Suspended Solids (ppm)</u>		<u>Sulfates (ppm)</u>	
	<u>Average</u>	<u>Maximum</u>	<u>Average</u>	<u>Maximum</u>
2/19-3/17/84	7	11	237	500
3/18-4/21/84	10	17	257	300
4/22-5/19/84	16	27	249	400
5/20-6/23/84	9	22	104	230
6/24-7/21/84	13	32	77	120
7/22-8/18/84	5	7	75	100
8/19-9/22/84	11	21	90	110
9/23-10/20/84	9	17	463	563
10/21-11/24/84	2	15	100	700
11/25-12/22/84	8	11	265	450
12/23-1/26/85	5	18	66	100
1/27-2/23/85	10	17	218	450
2/24-3/23/85	17	31	313	450
3/24-4/20/85	3	19	255	620

Source: Hercules Aerospace Company (Radford AAP)

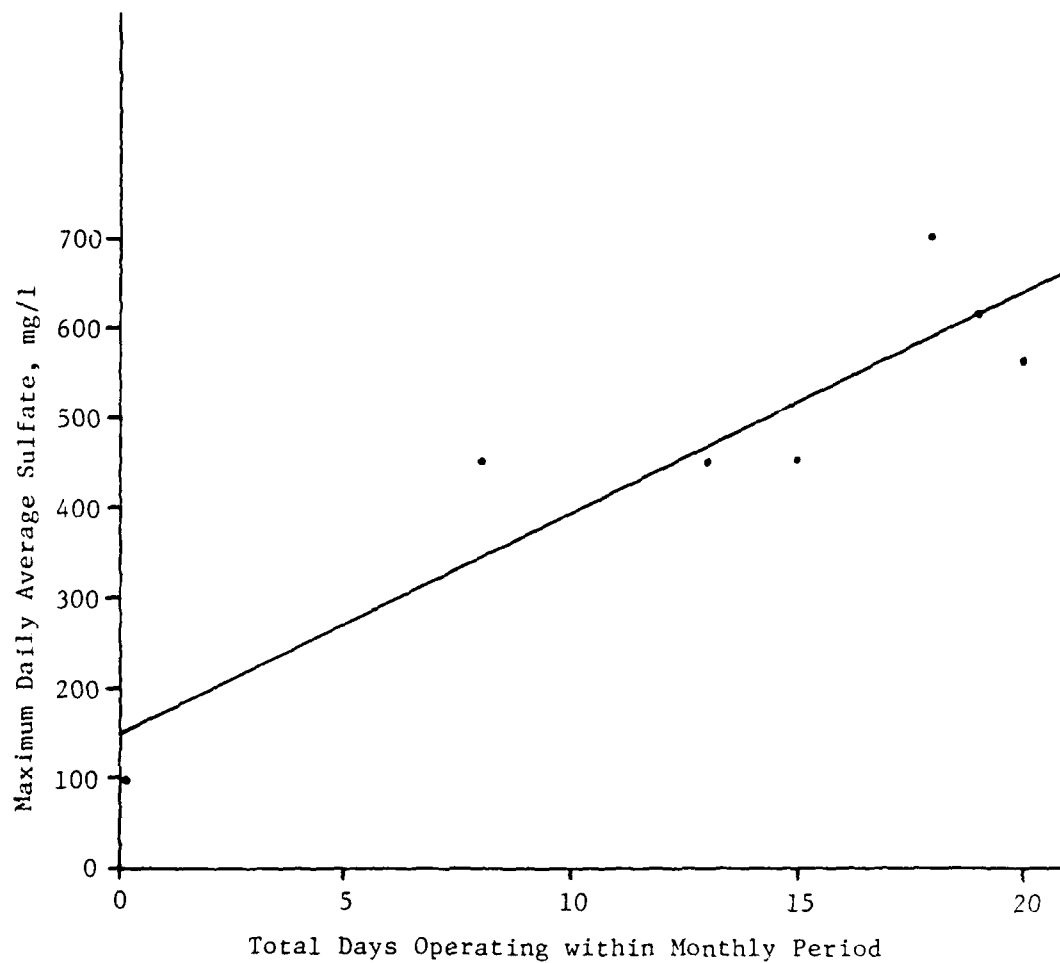


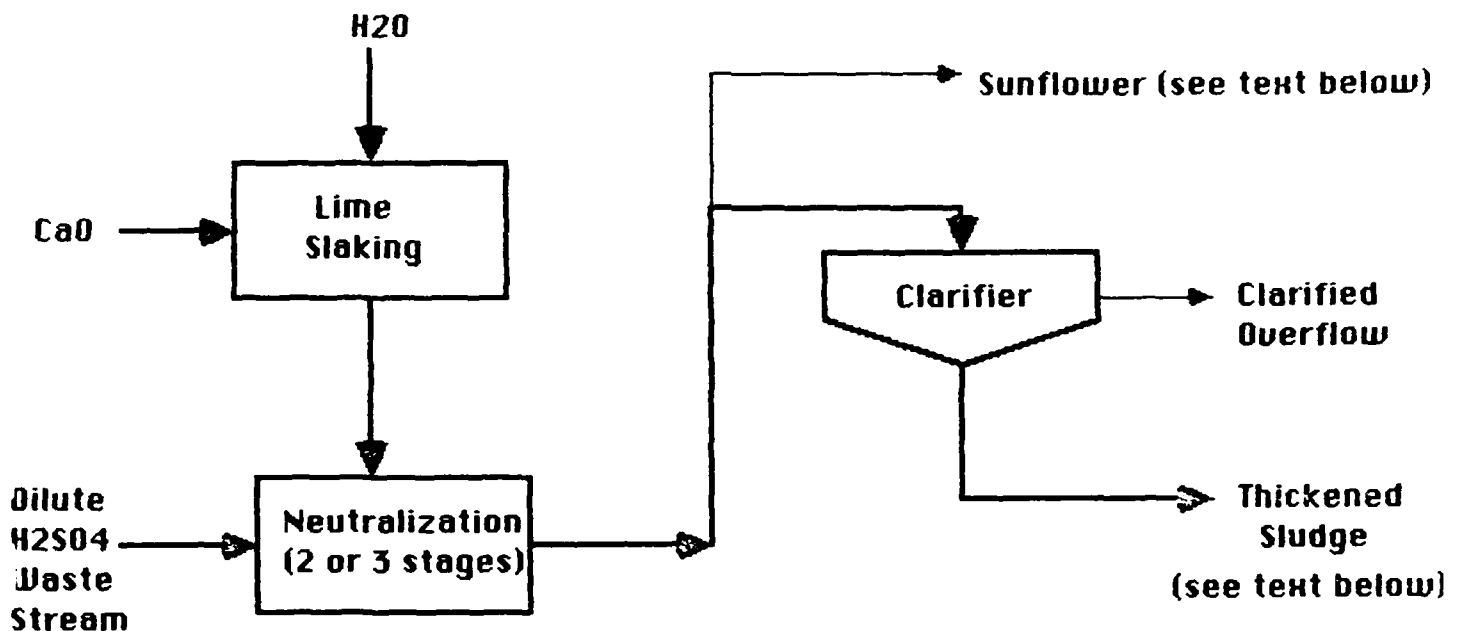
FIGURE 2-5

MAXIMUM 24-HOUR COMPOSITE SULFATE VS  
DAYS PER MONTH OPERATION OF SAR

Source: Arthur D. Little, Inc.

# Current Acid Wastewater Neutralization Practice at AAP s

FIGURE 2-6



<u>Plant Name</u>	<u>Plant Location</u>	<u>Ultimate Disposal of Thickened Sludge</u>	<u>Ultimate Disposal of Clarified Overflow</u>
Sunflower AAP	DeSoto, KS	No clarifier/thickener; neutralized wastewater to evaporation pond; theoretically no pond overflow.	
Newport AAP	Newport, IN	Storage lagoon; lagoon overflow to river.	Combined with other wastewaters; discharged to river.
Radford AAP	Radford, VA	Vacuum filtered; landfilled.	Combined with other wastewaters; discharged to river.
Volunteer AAP	Chattanooga, TN	Vacuum filtered; landfilled.	Double ion exchange; treated water recycled.*
Joliet AAP	Joliet, IL	Vacuum filtered; landfilled.	Barium carbonate precipitation; double ion exchange; treated water recycled.*

\*These wastewater treatment units were constructed after last SAR production run, therefore, they have never been operated.

Source: Arthur D. Little, Inc.

systems would theoretically permit total recycle of the water, i.e., zero discharge. These are discussed in more detail below.

#### 2.2.2 Ion Exchange - Volunteer AAP

Volunteer AAP is located a few miles northeast of Chattanooga, TN, just upstream from Chickamauga Dam. The treated effluent from their SAR waste treatment plant flows into Lake Chickamauga, which may be the reason the clarified lime neutralized effluent would be subjected to ion exchange to remove essentially all of the Ca and  $\text{SO}_4$  ions. We have not seen the documentation to confirm the reason for the ion exchange unit but understand that the state considers Lake Chickamauga to be a public supply for drinking water.

Figure 2-7 is a schematic flowsheet for the lime/ion exchange systems (Ref 46). The flow rates shown are not the design rates for Volunteer, but rather, for comparison, are based on the input flow rates of the Radford AAP SAR waste treatment facility. (All other flowsheets throughout this report are on the same basis.)

The advantages of the ion exchange system are:

- permits total water recycle, therefore, zero discharge is obtainable; and
- only a moderate increase in chemical cost is required.

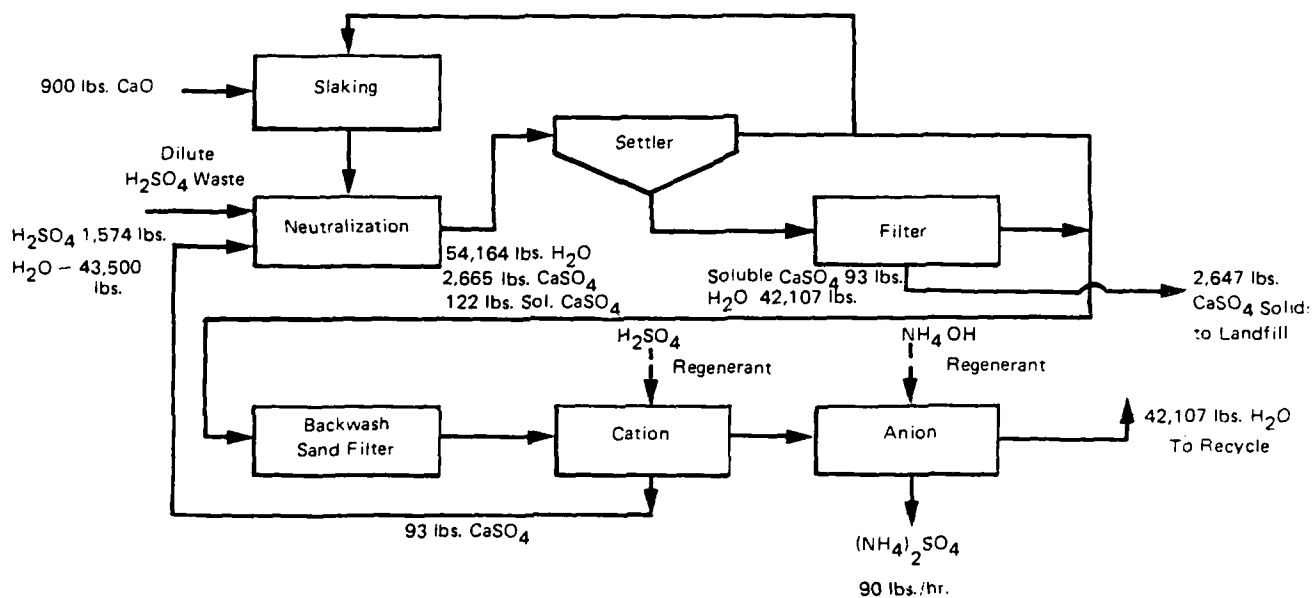
However, there are some legitimate concerns as to operation of this system.

- ability of cation exchange to remove high sulfate concentrations;
- dependence of the ion exchange system on good operation of the upstream lime precipitation system;
- the need for disposing of trivial amounts, 1 ton/day, of ammonium sulfate  $[(\text{NH}_4)_2\text{SO}_4]$  fertilizer byproduct; and
- to the extent that the ammonium sulfate is used by local farmers, the  $\text{SO}_4$  will ultimately go back to the same river, so that the ion exchange has achieved no net improvement in the local environment.

#### 2.2.3 Barium Precipitation with Ion Exchange - Joliet AAP

This process, Figure 2-8, is like the ion exchange process described above but with the addition of barium carbonate ( $\text{BaCO}_3$ ) precipitation of the soluble sulfate from the clarified thickener overflow before it is sent to the deionization units. The barium carbonate causes the soluble Ca ions to precipitate as calcium carbonate ( $\text{CaCO}_3$ ) and the soluble  $\text{SO}_4$  ions to precipitate as barium sulfate ( $\text{BaSO}_4$ ). This reduces the soluble salts load to the ion exchanger by a factor of 100. This process was installed in the mid-1970s but never operated.

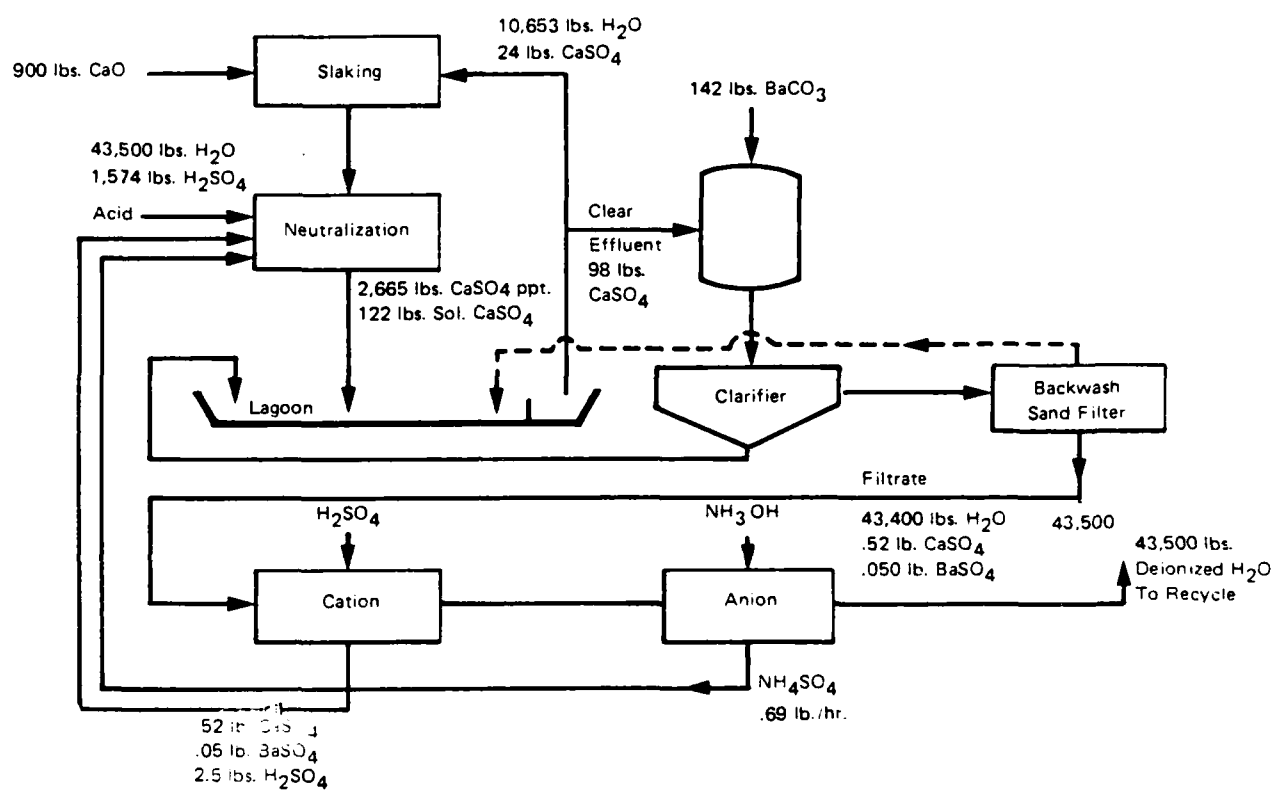
FIGURE 2-7  
ION EXCHANGE



Source: Arthur D. Little, Inc.

FIGURE 2-8

BARIUM PRECIPITATION PLUS ION EXCHANGE



Source: Arthur D. Little, Inc.

The advantages of this process are that it:

- permits total water recycle, therefore zero discharge is obtainable;
- greatly reduces load to ion exchange unit and, therefore, decreases the size and capital cost of the ion exchange systems; and
- essentially eliminates  $[(\text{NH}_4)_2\text{SO}_4]$  disposal problem.

The chief concerns for this process are:

- high chemical cost of  $\text{BaCO}_3$  precipitant;
- dependence on good operation of the upstream lime precipitation system; and
- even though barium sulfate is innocuous, barium in any form (the way the law reads) becomes a Resource Conservation and Recovery Act (RCRA) waste. Thus, with the current process layout, the main gypsum lagoon would become contaminated with  $\text{BaSO}_4$  and become a RCRA site.

#### 2.2.4 EPA and State Standards for Soluble Sulfate

EPA's Standards are based on receiving stream's ability to dilute the sulfate to acceptable concentrations. Current stream standards are:

- General 500 ppm  $\text{CaSO}_4$
- Drinking Water 250 ppm  $\text{CaSO}_4$

The drinking water standards apply if discharge is within five miles upstream of a public water supply intake.

An example of a receiving stream being used to its full absorptive capacity in establishing sulfate limits for an AAP is given by Sunflower AAP, which discharges into the Kansas River (see below).

#### Kansas River Absorptive Capacity:

$$(250 - 214) \text{ ppm} \times 644 \text{ ft}^3/\text{sec} \times \frac{3,600 \times 24 \times 62.4}{10^6} = 124,900 \text{ lb/day} \\ (56,670 \text{ kg/day})$$

river  
upper  
limit

95 percentile  
upstream  
conc.  $7Q_{10}$

conversion  
factors

Sunflower AAP Maximum Discharge Allowance:

$$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ 1626 \text{ ppm} & \times 9.2 \text{ MM gal/day} & \times \frac{8.33}{10^6} = 124,900 \text{ lb/day} \\ \text{max.} & \text{max.} & \text{conversion} \\ \text{conc.} & \text{flow} & \text{factors} \\ \text{allowed} & \text{allowed} & \end{array} \quad (56,670 \text{ kg/day})$$

However, a river's total absorptive capacity may not be available to an AAP. An example of this is given by Radford AAP which discharges into the New River (see below):

New River Absorptive Capacity:

$$(250 - 22) \text{ ppm} \times 756 \text{ ft}^3/\text{sec} \times \frac{3,600 \times 24 \times 62.4}{10^6} = 929,297 \text{ lb/day} \quad (421,641 \text{ kg/day})$$

Radford AAP Maximum Discharge Allowance:

Discharge Point	Description	kg/day	
		Avg.	Max
004	"C" Line	1,320	1,350
007	"A" & "B" Lines	37,000	40,000
012	TNT	2,400	6,000
029	Biol. Waste Treat.	3,000	6,000
---	Other discharges	6,280	21,650
---	with		
---	No Indiv. Limits		
		50,000	75,000
1985 Actual operating experience:			
Worst month		26,000	
Maximum daily			42,000

The "C" line above is the outfall from the SAR lime precipitation waste treatment plant. Here it can be seen that in addition to an overall plant upper limit for soluble sulfate, the individual stream 004 from "C" line, because of its rather advanced waste treatment system, has a severe point source limitation of only 1350 kg/day of soluble sulfate (and a maximum concentration of only 2300 ppm which is not shown on the above table).

Other states have a rather lenient enforcement policy vis-a-vis soluble sulfate as exemplified by the Sunflower example cited above.

Table 2-4 summarizes the soluble sulfate standards for five of the AAP that have SARs.



TABLE 2-4

STATE ENVIRONMENTAL DISCHARGE REGULATIONS  
FOR SOLUBLE SULFATE

<u>AAP</u>	<u>Receiving River</u>	<u>River Limit</u> ppm	<u>AAP Discharge Limit</u>
Radford	New	250	2975 lbs/day; 2300 mg/l <sup>(1)</sup> 50,000 kg/day avg; <sup>(2)</sup> 75,000 kg/day max.
Volunteer	Chickamauga Lake (Tennessee)	250	1977: 4200 lbs/day; 250 ppm  1985: Non-operating permit only; no sulfate limit
Newport	Wabash	500	1973: 1345 lbs/day 400 mg/l max  1985: Non-operating permit only; 2000 ppm D.S. (~80% CaSO <sub>4</sub> )
Joliet	Des Plaines	500	Not specifically stated <sup>(3)</sup>
Sunflower	Kansas	250	1626 ppm when operating

(1) "C" line only

(2) Total plant

(3) "The effluent sulfate concentration in the subject discharge shall be limited to a level that will not cause the receiving stream to exceed water quality standard in Rule 302.208 of the Illinois Pollution Control Board, Subtitle C, Rules and Regulations."

Source: Arthur D. Little, Inc.

### 2.3 Other Industries

Three major segments of the chemical industry are concerned with having to neutralize waste streams of sulfuric acid. In order of increasing volume of acid to be neutralized at a specific site, they are:

1. The sulfuric acid manufacturing industry;
2. Titania plants using the sulfate (sulfuric acid) process; and
3. Phosphate fertilizer plants.

We have contacted plants, in each of these three industries, that we felt would most likely have advanced waste treatment systems for their acid waste. Our findings are discussed below:

#### 2.3.1 Sulfuric Acid Plants

There are approximately 140 sulfuric acid plants in the United States, including captive, partly captive and commercial plants. Those that burn elemental sulfur have a negative water balance, i.e. they have a net consumption of process water so that there is no acid waste stream to treat and dispose of. However, those plants that burn sludges (mixtures of oil, water and spent recycled sulfuric acid) have a net excess of water which means they have a dilute acid stream which requires treatment and/or disposal. In an attempt to find advanced waste treatment technologies, we contacted most (eight) of the significant size sulfuric acid plants that burn high percentages of sludges. A brief summary description of each plant's waste treatment system follows:

PLANT 1: Sulfuric acid plant in Texas that burns 95% sludge.

The plant's environmental coordinator described their process as follows: the acid produced from sludge burning from the alkylation process is strengthened with additional sulfuric acid and sent back for reuse. Consequently, there is little excess waste sulfuric acid to deal with. He went on to mention that they do use sodium hydroxide (NaOH) and  $H_2SO_4$  addition in the wastewater treatment process to automatically control pH; this being the only waste treatment required.

PLANT 2: Sulfuric acid plant in Louisiana that burns 83% sludge.

The process described by the manager of Environmental Services involves neutralization of the final waste. The combustion off-gas from the sludge burning process is scrubbed with water in a Peabody Process Systems' scrubber with the scrubber effluent sent to a wastewater tank for neutralization with NaOH. The wastewater is maintained as neutral as possible (a pH of 7 to 8). The contents of the tank are not checked after neutralization but are sent to a biological treatment plant prior to being discharged to the river (NPDES discharge).

PLANT 3: Sulfuric acid plant in Kansas that burns 10% sludge.

The plant manager reported that this plant recycles the more concentrated of their "dilute" waste acid streams to a concentrator.

The final dilute waste stream, however, is handled in a batch neutralization with lime, followed by solids settling and landfilling of the resultant  $\text{CaSO}_4$  sludge. His observation was that there was not a single current neutralization method that is ideal and that when possible, dilute acid waste streams should be recycled back to the process.

PLANT 4: Sulfuric acid plant in Ohio that burns 55% sludge.

The combustion off-gas from the sludge burning process is cooled by a direct water spray; condensate formed creates a dilute acid stream. The acid stream is then further diluted by the addition of other wastewater. Caustic is metered into the stream to bring the pH up to 2.0, i.e. a 0.2 percent acid. The resultant solution is shipped to SOHIO for disposal.

The plant engineer went on to mention that using caustic is more costly than lime.

PLANT 5: Sulfuric acid plant in Pennsylvania that burns 56% sludge.

The wastewater generated at this plant is treated in a batch neutralization process. The products from the sludge burning, sulfur dioxide ( $\text{SO}_2$ ) and sulfur trioxide ( $\text{SO}_3$ ), are scrubbed with water and the product is a strong 10% acid stream. This acid stream is small in volume, about 100 gal/min. The stream is then mixed with 500 gal/min of other waste and diluted. The total waste stream (600 gal/min) is stored in 24 hour detention (equalization) tanks where caustic is introduced by both automatic and manual feed transmitters and the pH monitored.

After equalization, the waste goes through various other processes including oxidation, clarification, biofiltration and fluorination prior to being discharged to a stream which feeds into the Allegheny River.

PLANT 6: Sulfuric acid plant in New Jersey that burns 90% sludge.

The supervisor of environmental affairs advised us that this plant no longer burns sludge (since the spring of 1981). He reported that they do use caustic for the neutralization of their presumably minor residual acid waste stream, but would not go into any further details about the process itself. He commented on the benefits of NaOH neutralization and the drawbacks of CaO precipitation (i.e., elimination of lime slaking and the need for disposal of calcium sulfate sludge).

PLANT 7: Sulfuric acid plant in Indiana that burns 60% sludge.

The technical superintendent described the acid plant's wastewater treatment process as being one very similar to that which is employed at Radford AAP. Calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ] or CaO is added to the dilute acid stream such that a slurry, neutralized to a controlled pH, is formed. The neutralized slurry is then sent to a clarifier. The clarified liquor is recycled back to the process while the  $\text{CaSO}_4$  cake formed is landfilled.

Two other technologies were also discussed. One involves adding magnesium oxide ( $\text{MgO}$ ) to the acid stream forming magnesium sulfate ( $\text{MgSO}_4$ ), a useful product. He added, however, that this is a costly process. Another process used at their Louisiana plant basically involves increasing the acid strength and feeding it to an absorbing tower and then making other useful products (such as aluminum sulfate): the gases from the combustion of the sludge ( $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{NO}_2$ ) are sent to a scrubbing tower and scrubbed with water in which the dilute acid is formed. This acid is then strengthened to 20 percent and sent to an absorbing tower where other products can be formed. The technical superintendent indicated, however, that the major drawback to this method is that it is very energy intensive.

PLANT 8: Sulfuric acid plant in Louisiana that burns 60% sludge.

At this acid plant, the waste acid is neutralized with slaked lime. The slurry formed is then pH controlled; after which, it is sent to a clarifier and filtered.

In summary, it can be seen that sulfuric acid plants merely neutralize the acid with caustic or lime, forming in the first case soluble sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) which is discharged to a receiving stream, or in the second case calcium sulfate ( $\text{CaSO}_4$ ) which is landfilled. The one novel idea was to use magnesium oxide ( $\text{MgO}$ ) instead of lime ( $\text{CaO}$ ) to form  $\text{MgSO}_4$  (Epsom salts) which have slightly more value than ( $\text{CaSO}_4$ ), gypsum. Apparently, however, this is an expensive, energy intensive process and is not commercially viable.

### 2.3.2 Titania Plants

By 1981 there were only three titania plants using the sulfate process. This process generates 4 1/2 tons calcium sulfate (gypsum) per ton of titanium oxide ( $\text{TiO}_2$ ) produced. Because of the sheer magnitude of the calcium sulfate disposal problem, one plant in New Jersey was forced to shut down for lack of finding sufficient landfill area for the waste gypsum. A second plant in Maryland has a proprietary process for removing the iron impurities from its waste gypsum (thereby improving its quality) which it then sells across the fence to a gypsum board plant.

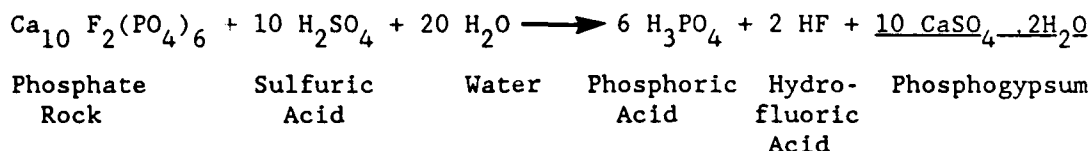
We were not able to verify the current waste treatment process used by the third titania plant employing the sulfate process. At one time they advertised a process for pelletizing the gypsum then drying it to make it suitable for feed to a cement mill (apparently cement can use up to 5%  $\text{CaSO}_4$ ) (Ref 7). We do not believe, however, that this process has ever been commercialized.

### 2.3.3 Phosphate Fertilizer Industry

Phosphate fertilizers are made by reacting phosphate rock with sulfuric acid to make phosphoric acid ( $\text{H}_3\text{PO}_4$ ) which is then reacted with more rock to make super phosphate fertilizers. The fertilizer plants are very large and therefore operate their own sulfuric acid plants which

range on the order of 1000 to 2000 tons of sulfuric acid/day rated capacity.

The primary reaction is:



For our purposes the process could be viewed as one where sulfuric acid is neutralized using phosphate rock rather than lime. Although the resulting calcium sulfate (referred to as phosphogypsum because of phosphate impurities) is a waste product, it is the largest product by tonnage and volume, with plants generating as much as 10,000 tons/day. The present stockpile in Florida alone is 400 million tons with the estimated pile by the year 2000 at one billion tons (Ref 32). By contrast, the lime precipitation plant at Radford generates 32 tons/day at capacity operation.

The EPA point discharge standards for these plants are concerned with phosphorous, fluorides, total suspended solids and pH. The only concern with the  $\text{CaSO}_4$  (gypsum) is the enormity of the piles and treating the rain runoff from these piles. [This is at variance with several of the AAP's experience where the state or regional EPA have set soluble sulfate limits.]

A modern phosphate fertilizer plant will have a negative water balance, i.e. there is no need to discharge water and they operate with a zero discharge permit from the EPA. Again, the only concern with these plants is treating the rain runoff from the plants' gypsum piles (Refs 33 and 34). The treatment of this runoff involves further liming for phosphate, fluoride and pH control only; apparently soluble sulfates are not of concern.

#### 2.3.4 Conclusions

In summary, among the major chemical industry segments that have significant sulfuric acid neutralization problems, we have noted the following:

1. The most common treatment process is straight neutralization with caustic or lime.
2. pH and turbidity are the chief parameters of concern.
3. We have seen no concern for soluble sulfate as a consequence of neutralization of sulfuric acid wastewater with lime.
4. None of the companies queried are using or contemplating using any advanced wastewater treatment techniques.

As a result of the above, we made no visits to industrial waste treatment plants as the purpose would have been to observe, evaluate and gain further insight into advanced waste treatment systems.

## 2.4 Solid Waste (Gypsum) Disposal or Reuse

In view of the concentration of the phosphate fertilizer industry in Florida and the prodigious files of gypsum accumulating there, it is not surprising that an industry sponsored state research institute, the Florida Institute of Phosphate Research, should spearhead research in this country on uses for waste gypsum or phosphogypsum. They have published a recent review of historic and current work on finding uses (chemical transformations or reuse per se) for phosphogypsum (Ref 32).

Also, in April of this year, they presented a paper at the American Institute of Chemical Engineers (AIChE) meeting in conjunction with investigators at Davy McKee who are funded by the Institute to do pilot work on conversion of gypsum back to sulfur or sulfuric acid (Ref 30).

In summary, the uses of calcium sulfate, per se, (gypsum or phosphogypsum) include:

- addition to cement (it can be used up to 5% concentration);
- raw material for manufacture of gypsum wall board;
- use in agricultural as a conditioner for sodic (high sodium) soils and as an additive to fertilizer for certain crops, like peanuts; and
- use as an aggregate in road building.

The primary problem associated with all of these uses is that the gypsum must be dried (for ease of handling and reduced transportation cost), which is a very energy intensive process.

Research on chemical uses of gypsum are primarily concerned with reduction to sulfur or  $\text{SO}_2$ . Because of the complexity of reducing all the way to sulfur, current research concentrates on mere reduction to  $\text{SO}_2$ , hence, reoxidation to  $\text{SO}_3$  and finally sulfuric acid. The chemistry to  $\text{SO}_2$  in simplified form is:



There are several processes that carry out this basic chemistry.

### Process

### Products

OSU-Krupp  
Iowa State University  
Davy McKee

Cement and sulfuric acid  
Lime and sulfuric acid  
Aggregate and sulfuric acid

The solid product from the process is controlled by the mix of impurities (pyrites, etc.) deliberately introduced into the front end of the process with the  $\text{CaSO}_4$ .

The U.S. Army Research and Development Center, Dover, NJ, is sponsoring work on the Iowa State University process that is monitored by Radford AAP (Ref 35).

At the current sulfur (or sulfuric acid), lime and cement prices, none of the above processes are economically viable. In Florida, there is a unique situation of essentially no aggregate (for road building) and a ready market for sulfuric acid. When Frasch sulfur begins to be depleted (projected 1990s), then the gypsum to aggregate and sulfuric acid process may be the first to become viable in the United States. <sup>(1)</sup>

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(1) As this report went to press we were informed by Radford AAP staff of a newly issued report: U.S. Army Armament Research and Development Center (Contractor Report ARAED-CR-86-86005) "Disposal of Waste Treatment Sludge." As we understand it, Radford staff, jointly with the Iowa State researchers, calculate that given adequate credits for lime and sulfuric acid, and solid waste disposal, etc., the Iowa State Process is economic, i.e., has a 10-year payout if operated at design capacity for the 10 years.

## SECTION 3

### ALTERNATIVE WASTE ACID NEUTRALIZATION SYSTEMS

#### 3.1 Systems Evaluated

One of the objectives of this study was to compare existing waste treatment processes for dilute sulfuric acid streams with advanced state-of-the-art and possible conceptual processes. Illustrated in Figure 3-1 are simple schematics of three existing processes and five state-of-the-art waste treatment technologies.

Of the three existing processes (1 to 3), Process 1 is the standard Radford AAP Lime Precipitation Process; Process 2 is essentially the system installed at Volunteer AAP; and Process 3 is generically that used at Joliet AAP (which is also geared to treat nitric acid ( $\text{HNO}_3$ ) waste). Both of these are actually advanced state-of-the-art processes, but have never operated at their designed commercial scale. Process 1 is described in Section 2.1.1; Processes 2 and 3 are described in Section 2.2.

Processes 4 to 8 contain state-of-the-art unit operations, but are conceptual processes in terms of combinations of operations and byproducts generated. These processes are described briefly below.

Processes 4 and 5. Proposed Processes 4 and 5 would employ lime neutralization like the previously described AAP processes. However, the clarifier overflow is reacted with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) to convert the soluble  $\text{CaSO}_4$  to  $\text{Na}_2\text{SO}_4$  and precipitating the  $\text{Ca}^{++}$  ion as insoluble calcium carbonate ( $\text{CaCO}_3$ ). This permits concentrating the  $\text{SO}_4$  by vapor recompression evaporation (Process 4), or by reverse osmosis (Process 5). The water is then recycled, there is no effluent, and the soluble sulfate converted to  $\text{Na}_2\text{SO}_4$  for sale to Kraft mills. However in both of these processes, the bulk of the  $\text{SO}_4$  from the  $\text{H}_2\text{SO}_4$  waste ends up as  $\text{CaSO}_4$  sludge requiring landfilling.

Process 6 uses vapor recompression (VRC) evaporation to directly concentrate the dilute (1 to 3 % conc.)  $\text{H}_2\text{SO}_4$  acid stream. Both the water and the  $\text{H}_2\text{SO}_4$  are returned to the process.

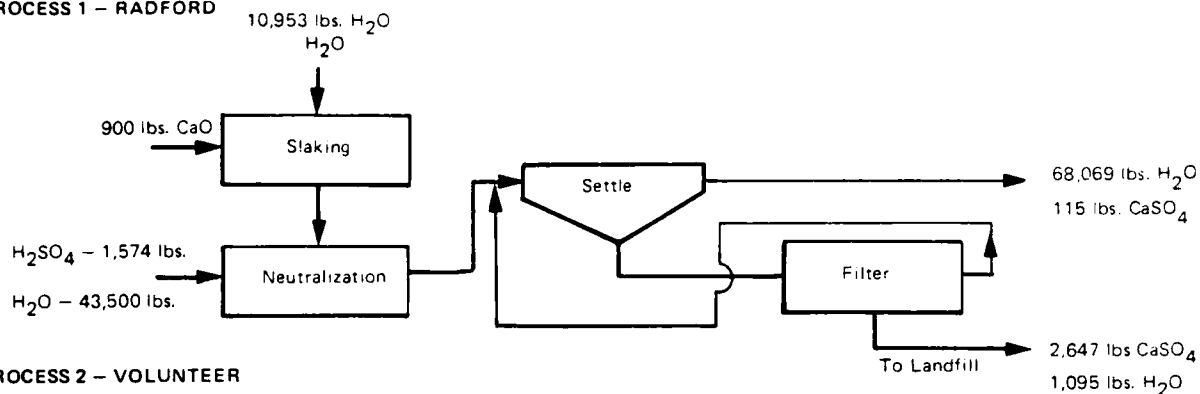
Process 7 first neutralizes the  $\text{H}_2\text{SO}_4$  using caustic, with concentration of resultant  $\text{Na}_2\text{SO}_4$  by vapor recompression evaporation. The water is returned to the process while the concentrated  $\text{Na}_2\text{SO}_4$  is sold to Kraft pulp mills.

Process 8 is a variation on Process 7; reverse osmosis (RO) is used to concentrate the  $\text{Na}_2\text{SO}_4$  stream somewhat to reduce the water load on the vapor recompression evaporation system.

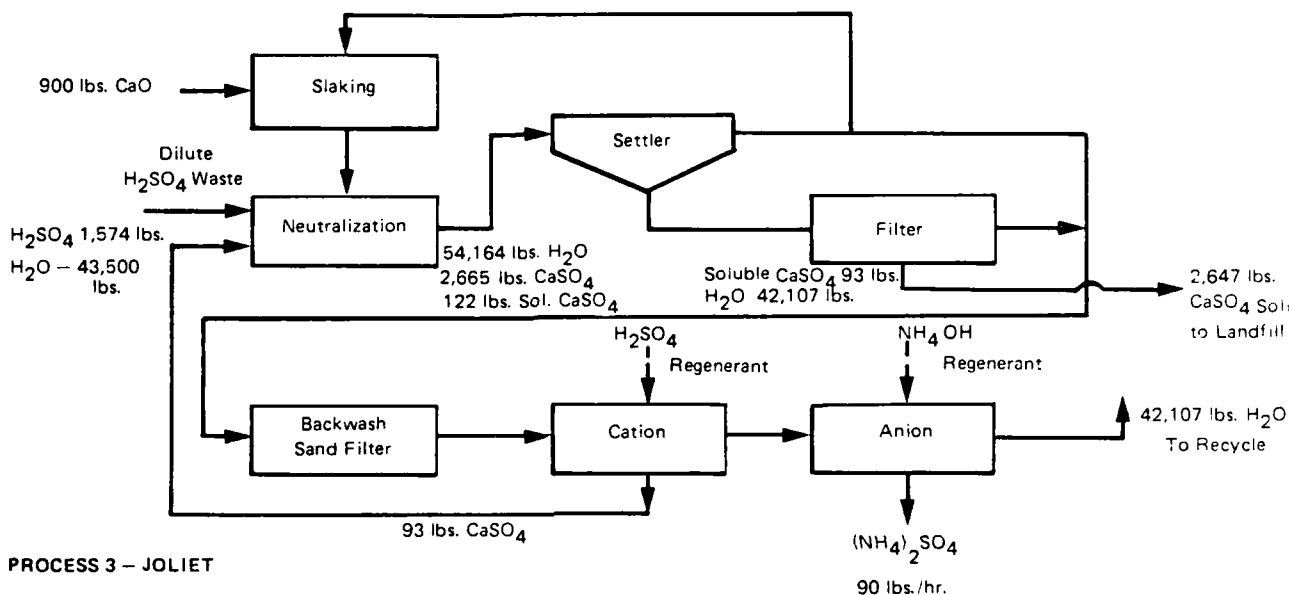
Material balances are shown around each of the eight processes of Figure 3-1. These are rough estimates based on the waste sulfuric acid stream rate calculated for Radford AAP, and on what we feel are



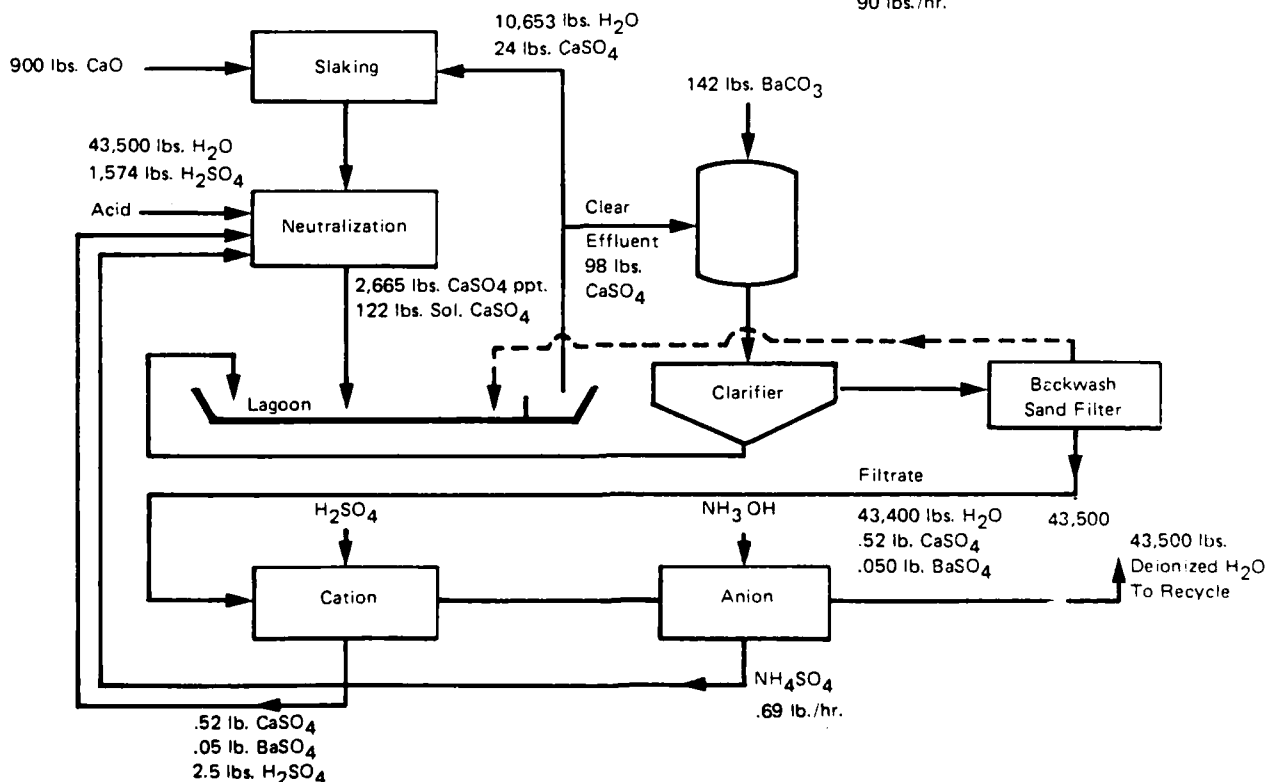
### PROCESS 1 - RADFORD



### PROCESS 2 - VOLUNTEER



### PROCESS 3 - JOLIET



(Basis: Design Flow Rates to Radford Process, lbs./hour)

# NEUTRALIZATION OPTIONS

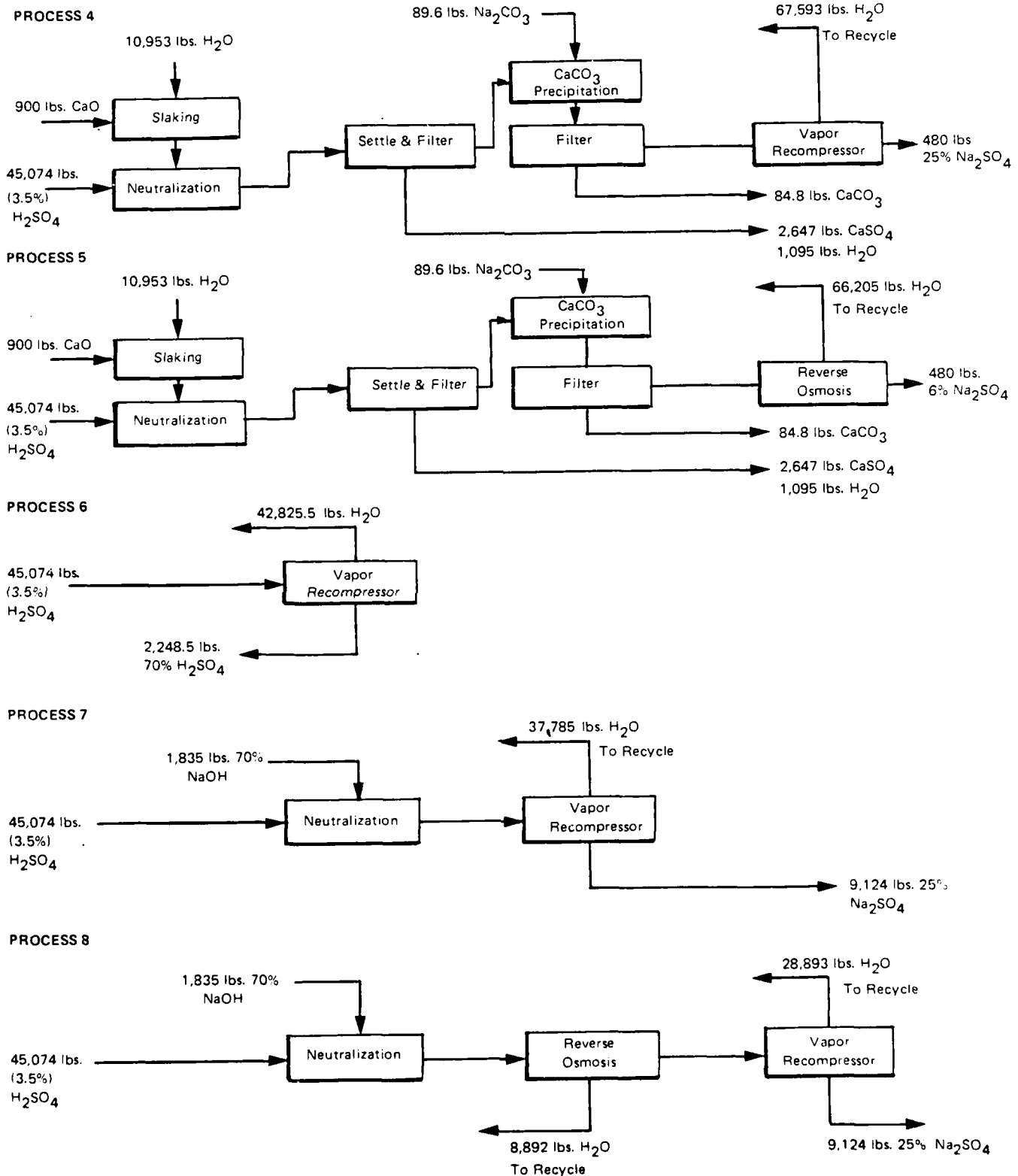


FIGURE 3-1 (Continued)

reasonable estimates of achievable performance across the reverse osmosis and vapor recompression units. The purpose in doing these material balances was to permit one to calculate rough estimates of capital and operating costs of the various unit operations based on the expected loads to them (discussed later).

### 3.2 Performance Criteria and Process Rankings

At the request of the Army, we developed a ranking system, using various "Performance Criteria" to come up with the one, or at most two, most promising processes. We proposed seven performance criteria with differing weighting scales, for which U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) concurred. These are summarized in Table 3-1, along with abbreviated notes to better describe the parameters.

Table 3-2 gives our ranking of the above eight processes using the performance criteria and weighting factors developed earlier. Process Number 6, which involves concentrating and ultimately recycling the sulfuric acid using vapor recompression evaporation ends up with a rating of 20 vs. 9 to 14 for the others. Four of the processes (1, 2, 7 and 8) have virtually the same rating 12 to 14, with three processes (3, 4 and 5) having low ratings of only 8 to 9.

Highlights of the process ratings by performance criteria are discussed below (immediately after Table 2).

- (a) "Ability to meet most stringent effluent limitations." All of the processes can have zero water discharge with the exception of the Radford AAP lime process, hence its low rating of only 2. Process 6, vapor recompression evaporation, was one rating below highest because of concern for the feasibility of mist carry-over given low pH values in the condensed water.
- (b) "Potential for resource recovery and conservation." Only Process 6 gets the highest rating as it is the only one to recover the original sulfuric acid. Processes 7 and 8 would recover sodium sulfate, but only at a significant expenditure for caustic.
- (c) "Potential for solids residual management problems." Only processes using vapor recompression evaporation, to recycle sulfuric acid or sell the sulfate values, receive a higher rating than the Radford AAP lime precipitation process which degrades the sulfate to gypsum for mere indefinite storage. We are suggesting here that the ion exchange processes and the processes recovering only small amounts of sodium sulfate probably create more of a solids disposal problem than the mere storage of gypsum, as the "solids" would be in concentrated liquor form.
- (d) "Operational reliability." Process 1, lime precipitation, is rated highest despite the seeming operating difficulties

TABLE 3-1

PROPOSED PERFORMANCE CRITERIA

<u>Criteria</u>	<u>Scale*</u>
(a) Ability to meet most stringent effluent limitations	0-5
(b) Potential for resource recovery and conservation	0-5
(c) Potential for solids residuals management problems	0-5
(d) Operational reliability	0-5
(e) Uniqueness of unit operations relative to current practice	0-2
(f) Relative annualized cost to employ strategy	0-3
(g) Overall environmental impact	0-5

TOTAL SCORE (Maximum 30)

---

\*Scale is additive with high score = good; thus very high cost = 0.

Source: Arthur D. Little, Inc.

### Notes to Table 3-1

(a) "Ability to Meet Most Stringent Effluent Limitations"

We believe that by the 1990's zero discharge of pollutants may be the most prevalent effluent limitation, which is reflected in our putting this at the top of the table of performance criteria.<sup>(1)</sup> The Radford AAP lime neutralization process can be improved with reductions in soluble sulfate ( $\text{SO}_4$ ) on the order of 30%, and for a non-noxious chemical, this may be considered adequate for most receiving streams in the Eastern United States. But in no way, without significant modification can this approach the spirit of "zero discharge".

(b) "Potential For Resource Recovery and Conservation"

Here we refer to reuse mainly at the plant site, i.e., there is no problem of having to sell or dispose of a by-product or waste product on the open market.

(c) "Solids Residual Management Problems"

Several existing processes generate  $\text{CaSO}_4$  (or  $\text{CaSO}_4/\text{CaCO}_3$ ) which has no value, but must be landfilled in lined ponds to keep it from entering drinking water sources. Other processes generate dilute  $\text{Na}_2\text{SO}_4$  solution, in small volume, which may make it difficult to sell or even give away to kraft mills, hence would be given very low ratings.

(d) "Operating Reliability"

This factor has to do with the complexity of the system, on-line factor for the individual unit operations, corrosiveness of the process, etc.

(e) "Uniqueness of Unit Operations Relative to Current Practice"

This has to do with supervision, maintenance, and operator familiarity with the unit operations relative to other units operations practiced at AAPs, and is intended to take into account the safety aspects as well.

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(1) Although the New Source Performance Standards (NSPS) and Best Available Technology (BAT) regulations requiring zero discharge (40CFR 415.212) were promulgated on March 12, 1974, these were subsequently remanded by the courts because no significant quantities of toxic pollutants were shown to be present as the result of EPA surveys. (Reference: Development Document for Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Industry - EPA 440/1-79/007 - June 1980 - p. 922). Nevertheless, changes in political climate and increased activity from environmental groups at specific sites may make zero discharge a choice to avoid further regulatory and legal action.

Notes to Table 3-1 (continued)

It has a maximum rating of only 2, reflecting the fact that management and operations at AAP's are trained to handle potentially more dangerous operations and are geared to the concept of adequate training and following Standard Operating Procedures (SOPs).

(f) "Relative Annualized Cost"

This category is self explanatory. We have presumed it appropriate to give this factor a slightly lower relative weighting, since Government departments would want to set an example of leadership in their waste treatment practices.

(g) "Overall Environmental Impact"

This factor, not intended to be "double accounting" with other factors, is intended to take into account the propensity for the proposed waste treatment process to inadvertently produce other, perhaps unanticipated adverse effects on the environment. We have alluded to the management headache of disposing of small quantities of dilute  $\text{Na}_2\text{SO}_4$  to the kraft mills. Also, say, because of a contamination due to a process upset, the final disposal of this dilute aqueous solution would represent a problem perhaps more serious than landfilling of precipitated  $\text{CaSO}_4$ . Again, use of barium as a precipitant (as provision is made for at Joliet AAP) may create more problems than it solves.

TABLE 3-2

PERFORMANCE CRITERIA RATINGS

(See Figure 1 and its notes for description of the Processes)

Criteria	Scale*	Process 1 (Radford)		Process 2 (Volunteer)		Process 3 (Joliet)		Process 4 (Lime & Soda & MVR)		Process 5 (Lime & Soda & RO)		Process 6 (MVR)		Process 7 (Soda & MVR)		Process 8 (Soda & RO & MVR)	
		Lime	Exchange	Lime	Exchange	Lime	Barium	Lime	Evap.	Lime	Evap.	Evap.	Evap.	Evap.	Evap.	Evap.	Evap.
(a) Ability to meet most stringent effluent limitations	0-5	2	5	5	5	5		5		5		4		5		5	
(b) Potential for resource recovery and conservation	0-5	0	1	1	1	1		1		1		5		2		2	
(c) Potential for solids residuals management problems	0-5	1	0	0	0	0		0		0		5		2		2	
(d) Operational reliability	0-5	4	3	3	2	2		2		1		2		3		1	
(e) Uniqueness of unit operations relative to current practice	0-2	2	1	1	1	1		0		0		0		0		0	
(f) Relative annualized cost to employ strategy	0-3	3	1	1	0	0		0		0		0		0		0	
(g) Overall environmental impact	0-5	1	1	1	0	0		1		1		4		2		2	
TOTAL SCORE (Maximum 30)		13	12	9	9	8		20		14		12		12			

\*Scale is additive with high score = good.

Source: Arthur D. Little, Inc.

experienced at Radford AAP. Processes 2, 3, 4 and 5 are mere add-ons to the Radford process--hence by definition more complex. The vapor recompression evaporation processes are rated lower because of concern for corrosion (Process 6) or erosion due to sodium sulfate solids entrainment (Processes 7 and 8) of the compressor turbine blades. Processes with reverse osmosis (Processes 5 and 8) have the lowest rating because of concern for membrane life and integrity (leaks).

- (e) "Uniqueness of unit operations relative to current practice." This criteria, as a whole, is weighted very low, its highest value being only 2 points (out of a maximum total of 30 for the seven criteria). The Radford AAP process has the highest rating, 2, the ion exchange processes 1, the evaporation process lowest at 0.
- (f) "Relative annualized cost to employ strategy." Again, this criterion carries a lower weighting factor, maximum of only 3. Six of the processes carry 0 rating, i.e., are expensive, compared to Radford AAP lime precipitation with the highest rating.
- (g) "Overall environmental impact." Here the barium carbonate precipitation process gets the lowest rating because of the concern of disposing of the barium sulfate waste and the concern that a process upset might result in exceeding the barium limits in the discharge water. The cation exchange unit should easily remove the small soluble barium ion from the solution. The simpler ion exchange process also gets a low rating because regenerating the anion exchange unit generates  $[(\text{NH}_4)_2\text{SO}_4]$  which would go back to the soil as fertilizer, the sulfate ultimately ending up in the rivers as before. The various sodium sulfate-end product processes get low ratings for the same reason; after one more use (kraft mills) the sulfate ends up in the river. Only Process 6, the vapor recompression evaporation process continually recycles the sulfate values, i.e., a unit of sulfate is re-used many times before ultimately being lost to the environment.

### 3.3 Cursory Economic Analysis

From the processes illustrated in Figure 3-1, we see that there are basically four unit operations to consider for advanced treatment systems for sulfuric acid waste:

1. Barium Precipitation,
2. Ion Exchange,
3. Reverse Osmosis, and
4. Vapor Recompression Evaporation.

The first two of these unit operations are concerned with removing the small residual soluble sulfate from the lime precipitation process, the



latter two concentrate the sulfate as sodium sulfate for sale as a byproduct. A fifth unit operation electrokinetic filtration would possibly achieve better filtration/dewatering of calcium sulfate and result in decreasing the cost of drying it, but the possibility of developing a market for this material is so low and the amounts involved at the AAPs so small, that we do not recommend carrying this forward as a candidate process alternative.

For cost estimating purposes we have used the following factors:

For Ion Exchange:

Cation resin - 1.9 meq/ml; \$75/ft<sup>3</sup>  
Anion resin - 1.6 meq/ml; \$180/ft<sup>3</sup>  
Cation regenerant (H<sub>2</sub>SO<sub>4</sub>); 200% excess required  
Anion regenerant (NaOH); 30% excess required

For Reverse Osmosis:

Capital cost = \$6.00/gal filtrate/day  
Operating cost = \$5.00/1000 gal filtrate

For Vapor Recompression Evaporation:

Capital cost = \$10.00/gal condensate/day  
Operating cost = \$8.00/1000 gal condensate

Table 3-3 summarizes our cost estimates for the various processes shown in Figure 3-1. As indicated by the various footnotes to the table, the costs are relative to (i.e. in addition to) the standard lime precipitation process as exemplified by the Radford AAP operation. To put them on a comparable basis, we have used the Radford AAP rate of waste generation as the basis. For example, Process 2 is indicated as generally similar to the Volunteer AAP waste acid process. Actually, the Volunteer AAP process receives nitric as well as sulfuric acid waste. Its waste treatment plant which includes a nitric acid reboiler and distillation column as well as lime precipitation and ion exchange, cost \$2.7 MM originally (1972) and was modernized for an additional \$2.2 MM in (1978). We estimate the ion exchange portion, scaled down to the quantity and concentration of Radford's H<sub>2</sub>SO<sub>4</sub> waste (1,575 lbs H<sub>2</sub>SO<sub>4</sub> in 43,500 lbs H<sub>2</sub>O compared to Volunteer's 2,354 lbs H<sub>2</sub>SO<sub>4</sub> in 80,500 lbs H<sub>2</sub>O), would cost only \$1.1MM in 1985 dollars.

We based the operating cost on 330 days/year operation, which would only be approached in a war emergency. We excluded the operating labor from all the processes since they would be roughly the same as for the base line process (lime precipitation). An exception might be Process 6, the simple vapor recompression evaporator with H<sub>2</sub>SO<sub>4</sub> recycle. Its labor might be significantly less.

We included the raw materials (lime) and utilities for operating the lime precipitation process to make valid comparisons with processes not using lime, i.e. Processes 6, 7, and 8.

TABLE 3-3

## WASTE SULFURIC ACID TREATMENT PROCESSES - ADDITIONAL COST OVER BASE CASE

	Process 1 (Radford) Lime	Process 2 (Volunteer) Lime & Ion Exchange	Process 3 (Joliet) Lime & Barium & Ion Exchange	Process 4 Lime & Soda & MVR Evaporation	Process 5 Lime & Soda & RO	Process 6 MVR Evaporation	Process 7 Soda & MVR Evaporation	Process 8 Soda & RO & MVR Evaporation
Capital Cost <sup>(1)</sup> , \$MM	Base Case	1.100	.6262	2.3351	.5752	2.920	1.400	1.589
Operating Cost <sup>(2)</sup> , \$1,000/yr								
Chemicals	114	213	418	164	164	---	809	809
Resins	---	19	1	---	---	---	---	---
Utilities	15	20	20	532	337	326	325	400
Maintenance	50	88	72	132	105	146	49	56
Gypsum Disposal	216	216	216	216	216	---	---	---
Depreciation @ 10%/yr <sup>(3)</sup>	---	110	62	233	157	292	140	159
Total Annualized Cost, \$1,000/yr	395	666	789	1277	979	764	1323	1424
Credits:								
Byproduct chemicals	---	---	---	24	0	380	821	821
Water recycled	---	---	---	16	16	11	9	9
Net Annualized Cost, \$1,000/yr	395	666	789	1237	963	373	493	594
Increased Cost Over Base Case, \$1,000/yr	0	271	394	842	568	(22)	98	199

- (1) Capital cost excluding cost of up-front standard lime precipitation (i.e. Radford AAP Process) for processes 2, 3, 4, and 5. However, no credit taken for eliminating the need for lime precipitation in processes 6, 7 and 8.
- (2) Assumes 24 hour/day, 330 days/year operation.
- (3) Excludes: (1) operating labor and associated overhead (all processes assumed equal at 2 persons/shift, and (2) depreciation of up-front lime precipitation system (for processes 1-5). Also does not include cost of capital employed.

Source: Arthur D. Little, Inc. Estimates from Table 1 of 12/2/85 Phase II report revised to include Maintenance and Gypsum disposal costs for processes 1-5.

It can be seen, on the last line of Table 3-3, that Process 6, vapor recompression evaporation of the raw  $\text{H}_2\text{SO}_4$  acid stream, and Process 2, simple ion exchange of the clarified lime neutralized water, appear to have the lowest annual costs.

A brief summary discussion of the eight processes follows, starting with the least promising.

Processes 4 and 5. Conversion of soluble  $\text{CaSO}_4$  to  $\text{Na}_2\text{SO}_4$ , thence concentration by vapor recompression evaporation (Process 4) or reverse osmosis (Process 5). The idea behind this process is to convert the  $\text{CaSO}_4$ , which has no economic value and is a bad scale former to  $\text{Na}_2\text{SO}_4$  which has no problems of scaling and could be sold to Kraft mills. However, the amount of Ca ion in the clarifier overflow is only 2,200 ppm or only 1 1/4 tons/day. At 330 days of operation this would generate only \$24,000/year byproduct income versus an operating cost of \$1,017,000 for vapor recompression evaporation (Process 4). Reverse osmosis (Process 5) is less capital intensive \$1.17 MM vs. \$1.93 MM for vapor recompression evaporation and the utility cost is lower, \$337,000/year vs. \$532,000/year, so that even though the recovered  $\text{Na}_2\text{SO}_4$  is more dilute (6% vs. 25%) and would have to be given away, the \$24,000 loss is negligible in view of the lower operating cost.

Processes 7 and 8. Total neutralization of the sulfuric acid waste by sodium carbonate followed by concentration by vapor recompression evaporation (Process 7) or reverse osmosis and vapor recompression evaporation (Process 8). These processes have the advantage of recovering all the sulfate value of the sulfuric waste stream (1,545 lb/hr versus only 82 lb/hr of sulfate from Process 1 the lime precipitation process). Furthermore the cost of the lime (\$114,000/year) is eliminated.

However the sodium carbonate used for the neutralization costs more than the value of the sodium sulfate byproduct generated (\$120/ton versus \$90/ton). Even so, these two processes give the lowest net chemical cost of any process but Process 6.

Examination of the data in Table 3-3 also shows that the use of reverse osmosis to reduce the electric load of the vapor recompression evaporation ends up with a net total increase in utility load and a higher capital cost, i.e., it has no advantages.

Processes 2 and 3. Standard lime precipitation plus ion exchange (Process 3-Volunteer) or barium precipitation plus ion exchange (Process 4-Joliet) to remove soluble sulfate. Process 3 along with Process 6 are the two least expensive means by which improvement over the standard lime precipitation process can be realized. Our accuracy of estimating is not sufficient to distinguish between the two processes. In Process 3, the water is totally deionized and therefore recyclable. However, the  $\text{CaSO}_4$  disposal problem remains, and in regenerating the anion resin using ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), ammonium sulfate is generated. Since no concentration facilities are provided it is assumed that this can be given away, at no cost, to local farmers.

We do not fully understand the advantage of putting a barium carbonate precipitation system upstream of the ion exchanger (Process 4). It reduces the size of the ion exchanger about 20 fold, but the cost of the barium carbonate consumed makes this an expensive substitution. The current staff at Joliet AAP do not fully understand the reasoning behind the barium precipitation system either, nor for that matter, the driving forces that caused the earlier staff to put in such a rigorous system for sulfate control. The Joliet AAP barium sulfate/ion exchange process was put in at the same time as the Volunteer AAP ion exchange plant, but designed by different branches of the Corps of Engineers and installed by different contractors. The current Joliet staff heard talk of the fact that, at the time, the Joliet designers were concerned that the anion unit could not adequately remove the high concentrations (1600 ppm) of  $\text{SO}_4$  involved. Better documentation would be helpful, but the process is subject to easy laboratory verification if deemed necessary.

Process 6. The vapor recompression evaporation process appears by far the simplest, i.e., by elimination of: 1) lime slaking, 2) neutralization, 3) precipitation, 4) settling and filtration and 5) solids disposal. Further, it has the potential for almost complete recovery of the sulfuric acid values in the waste stream, coupled with zero water discharge. All of these virtues are in large part offset by the fact that our preliminary rough cost estimates (Table 3-3) show this process to be by far the most capital and energy intensive; albeit on a simplistic annualized cost basis, and the assumption of operating at design capacity 330 days/yr, the process appears competitive with all the other alternatives to lime neutralization.<sup>(1)</sup> Because of these contrasting factors, this process was singled out for fine tuning the estimates of equipment size, electric load and capital cost. In addition, we used the Federal Government's method of making annualized cost comparisons. The studies are summarized in the next section.

#### 3.4 Re-examination of MVR Evaporation

Figure 3-2 shows a schematic diagram of a mechanical vapor recompression evaporator. The dilute sulfuric acid (1), enters the evaporator containing concentrated sulfuric acid, boiling off water at atmospheric pressure from concentrated acid (2). The high speed centrifugal compressor, operating over a 2:1 compression ratio, raises the pressure of the evaporated vapor (3), from 1 atmosphere to 2 atmospheres (approximately 30 psia). This compressed vapor (4) has a condensation

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(1) In a letter commenting on the rough draft of this report, the Maintenance and Power Supervisor at Joliet AAP strongly suggested that the typical low operating factors at AAPs requiring on/off operation of the sulfuric acid systems would aggravate the corrosion problem even further and, in his opinion, stronger emphasis should be given to that possibility. (Ref: Letter B.D. Troyer/N.A. Desmarais to D.J. Thompson, Contracting Officer's representative, Aug. 21, 1986)

## Mechanical Vapor Recompression Evaporator System for Concentrating 2 1/2% Sulfuric Acid

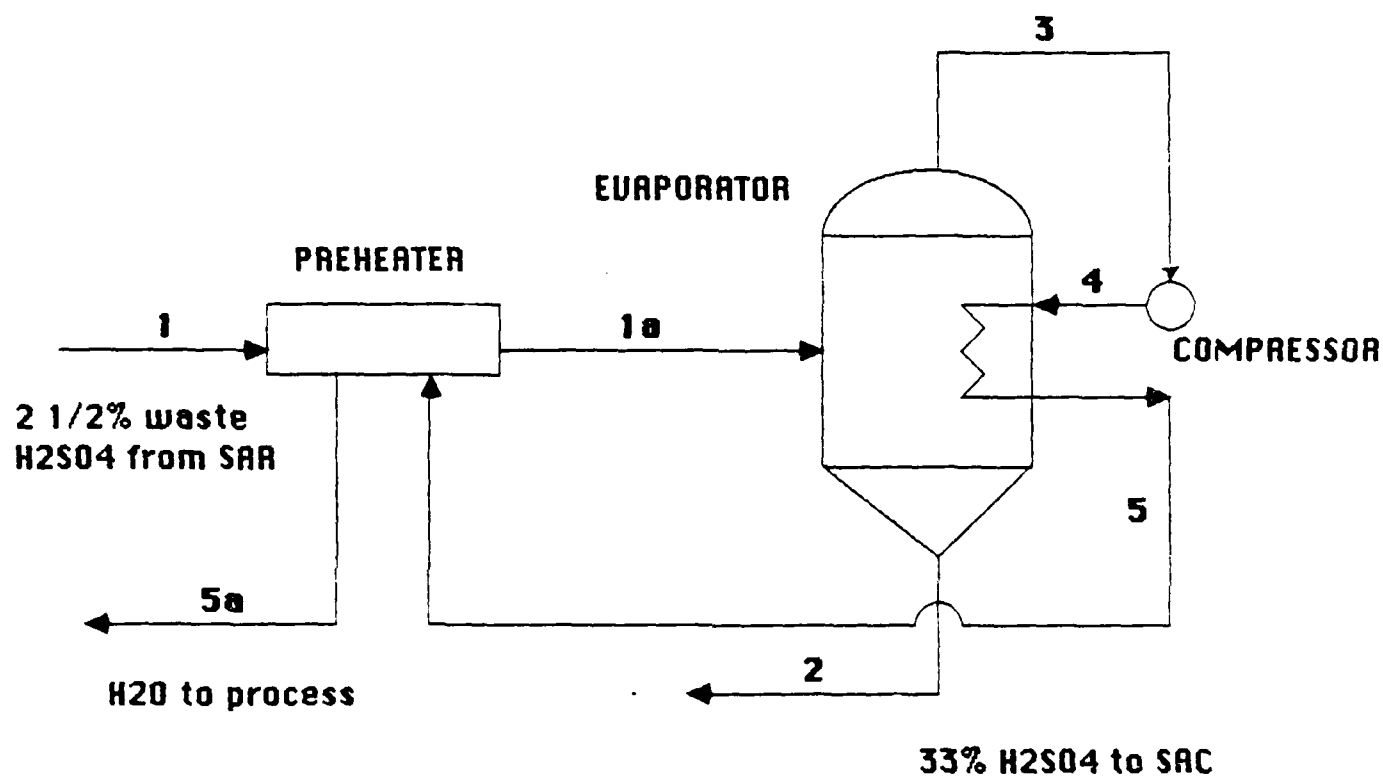


FIGURE 3-2

Source: Arthur D. Little, Inc.

temperature of 250°F, thus providing a  $\Delta T$  driving force (250-212=38°F) for evaporating more water, using the latent heat of condensation of this already evaporated water.

If there were no, or insignificant, boiling point rise due to increasing concentration of the solids, the water would boil at 212°F and in the vapor state at 1 atmosphere would have an enthalpy of 1150 Btu/lb. Adiabatic compression to 29.5 psia would raise the vapor's temperature to 330°F giving it a total enthalpy of 1205 Btu/lb. Thus, this two-atmosphere steam has roughly 40 Btu superheat and 945 Btu enthalpy of condensation for a total of 985 Btu/lb for evaporating additional water. All of this available evaporation energy was achieved by adding 55 Btu/lb to the 1 atmosphere steam via the centrifugal compressor; at 75% compressor efficiency this translates to  $55/0.75 = 73$  Btu/lb to achieve 985 Btu/lb water evaporative capacity. Compared to the simple one stage evaporator where roughly 1 lb of steam evaporates 1 lb of water, here we have 1 lb of steam evaporating 13 lb water ( $985/73 = 13.5$ ). Boiling point rise due to acid concentration, heat losses, and cold feed to the evaporator reduce this efficiency somewhat and are discussed below.

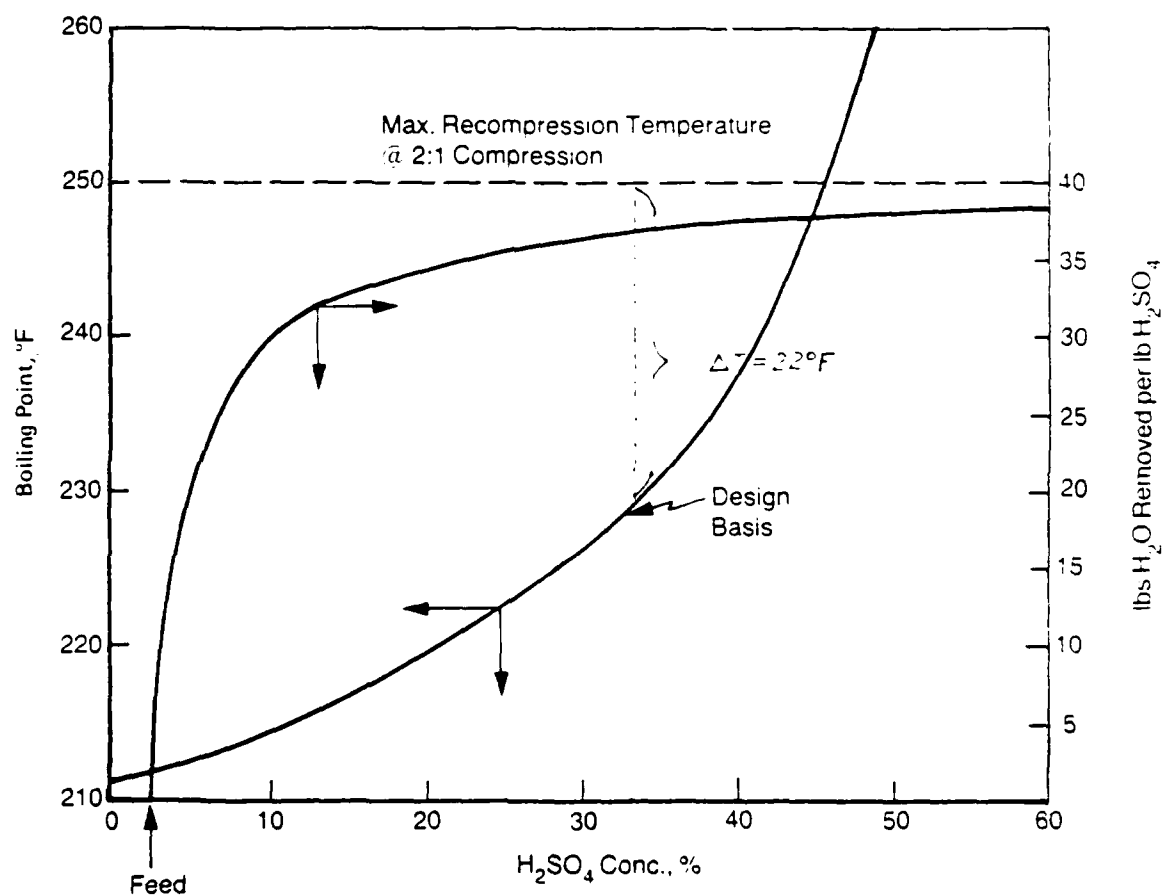
#### 3.4.1 Energy and Material Balance

Figure 3-3 shows: 1) the boiling point of sulfuric acid versus its concentration, and 2) the lbs of water removed per lb of sulfuric fed to an evaporator system, based on a feed of 2-1/2% concentration. Finally, for reference, we have indicated the condensation temperature corresponding to the maximum achievable pressure by a single stage centrifugal compressor operating at a 2:1 compression ratio from atmospheric pressure, namely 250°F.

Studying the chart, one observes that for 46% sulfuric acid concentration, the boiling point is approximately 250°F. If 250°F is also the condensation temperature for the heating medium, there would be no  $\Delta T$  driving force for heat transfer; thus, the heat transfer surface area required would be infinite.

From multiple effect evaporator practice a "rule of thumb" is to have a 20 to 22°F  $\Delta T$  per evaporator effect as a good compromise between equipment cost and energy savings. From Figure 3-3 this would suggest a boiling point of 250-22=238°F, giving a  $H_2SO_4$  concentration of only 33%. Although this is not as high a concentration acid as we would like (preferably 60 to 70% to feed directly to an SAR), we note, also from Figure 3-3, that in concentrating from 2½ to 33%, we have removed 37 lb  $H_2O$ /lb of acid, of the total 38.5 lbs/lb that we would desire for feeding to the SAR; i.e., 96% of the water load is removed by the MVR evaporator. Because of the small volume of the stream involved, this extra residual water should not be a significant extra water load to the SAR; if it is, this 33%  $H_2SO_4$  stream could first be fed to a conventional Sulfuric Acid Concentrator (SAC), to raise its strength to 60 to 70% concentration before going on to the SAR.

Figure 3-4, shows the material and energy balance for concentrating 2-1/2%  $H_2SO_4$  to 33%  $H_2SO_4$ . A trial and error solution is required to



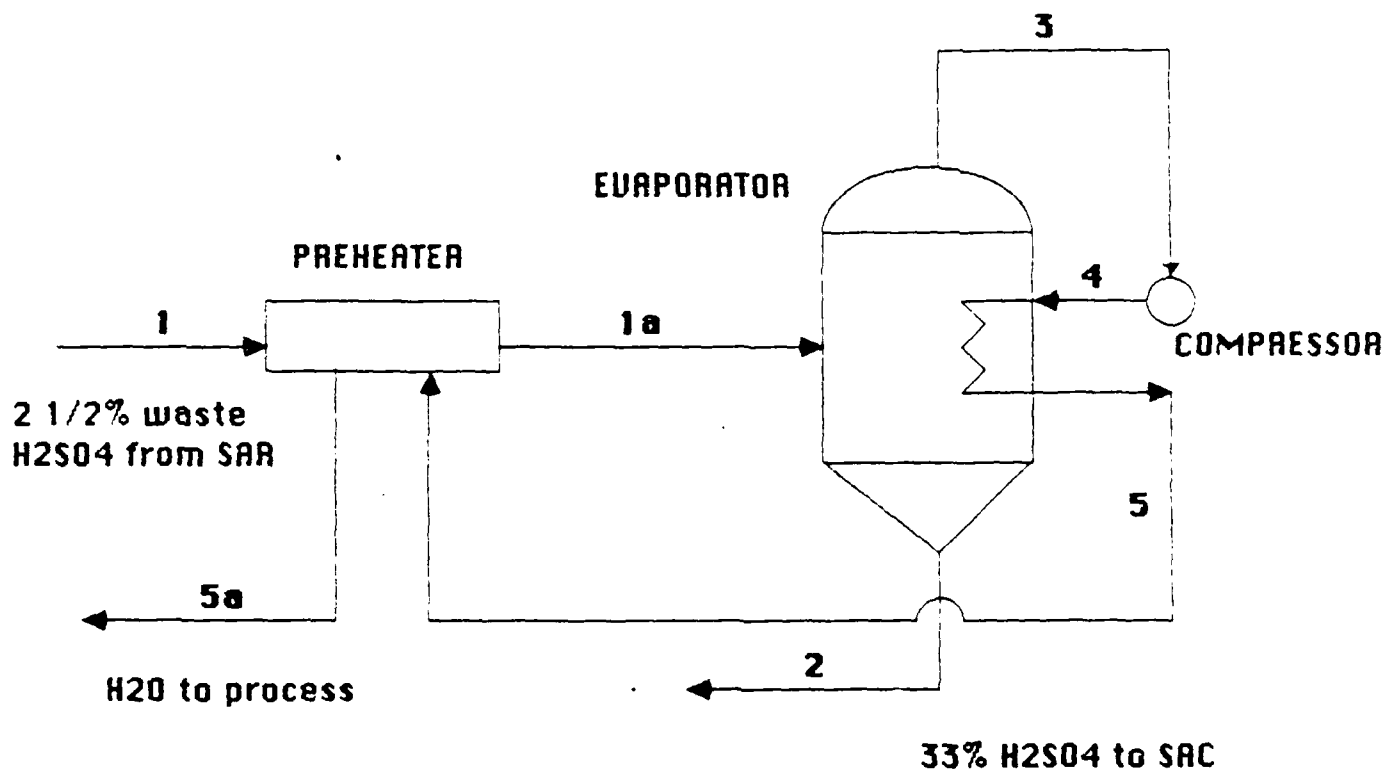
ACID CONCENTRATION VS B.P. AND EVAPORATION LOAD

FIGURE 3-3

Source: Arthur D. Little, Inc.

FIGURE 3-4

# MUR EVAPORATOR SYSTEM FOR CONCENTRATING 2 1/2% H<sub>2</sub>SO<sub>4</sub>



	Stream Number						
	1	1a	2	3	4	5	5a
H <sub>2</sub> SO <sub>4</sub> conc. (%)	2.5%	2.5	33	0	0	0	0
H <sub>2</sub> O conc. (%)	97.5	97.5	67	100	100	100	100
Pressure psia	14.7	14.7	14.7	14.7	30	30	30
State	liq	liq	liq	gas (16°SH)	gas (100°SH)	liq	liq
Temp (°F)	65	195	228	228	350	250	117
Enthalpy (Btu/lb)	28	157	43	1157	1214	(Vapor 1164) Liq 219	85
Flow (lb/hr)	45,074	45,074	4770	40,304	40,304	40,304	40,304

SH = Superheat

Source: Arthur D. Little, Inc.



balance the heat conservation of the preheater with the load applied to the compressor.<sup>(1)</sup> At 75% compressor and driver efficiencies, this load equates to 802 kW or 1076 HP. The compressor would have to handle 13,500 ft<sup>3</sup>/min actual compressed vapor.<sup>3</sup> Single stage centrifugal compressors are available to 100,000 ft<sup>3</sup>/min.

#### 3.4.2 Process Economics

Our original capital cost for the MVR evaporator process, for comparison with the other seven processes discussed above, was based on a "rule of thumb" analogy from water desalination practice of \$10 Capital Investment/gal per day of evaporative capacity. For roughly 43,000 lb/hr capacity, this gave \$1.3 MM standard cost which we then multiplied by 2.25 (to allow for the extra cost of high alloy steel, and tantalum for the turbine blades, compared to the 90:10 copper, steel, epoxy coated steels and aluminums, etc. used in saline water purification service) for a total cost of \$2.93 MM. As an aside, the Technical Director of Atlas Copco, a manufacturer of compressors for this service, published a paper on the economics of mechanical vapor recompression evaporation (Ref 39). He used as an example a capacity of 50,000 lb/hr (versus our revised 40,300 lb/hr) evaporative load and came up with the same \$1.3 MM estimated cost for his system as we did by rule of thumb for our albeit slightly smaller system.

As a result we elected to continue to use our original estimated cost (\$1.3 MM x 2.25 = \$2.93 MM), to give extra allowances for potential corrosion problems.

Table 3-4 shows a breakdown of the operating cost of the two processes to be compared: MVR evaporation for recycle of sulfuric acid versus the standard lime neutralization process. Here we have assumed the MVR evaporator would be located in, and integrated with, either the SAR or SAC facilities, thus requiring only one operator/shift (actually less than one) whereas lime precipitation is a stand alone isolated waste treatment plant requiring two operators/shift (for safety and work load).

Next to operating labor, disposal of gypsum is the single largest cost of the lime precipitation process (estimated by Hercules Aerospace Co. based on current practice at Radford AAP). Cost of electricity dominates the operating cost for the MVR evaporation system. The recovered sulfuric acid, because it would be at only 33% concentration, was credited at only \$50/ton, versus market price of \$72 to 80/ton for 98% acid. (If it were necessary to send the 33% acid to a SAC for further concentration before going to the SAR, its byproduct value would be only on the order of \$30/ton.) Using the average electricity cost at

---

(1) The material balance shown gives a compressor adiabatic load of 57 Btu/lb vapor which is 2 to 11 Btu/lb excess over that required for the evaporation depending on the useful degree of superheat of vapor from the concentrated acid.

TABLE 3-4

CALCULATION OF ANNUAL OPERATING COSTS: MECHANICAL VAPOR RECOMPRESSION  
EVAPORATION VS. EXISTING LIME PRECIPITATION SYSTEM

Process 1 - Lime Precipitation		Process 6 - MVR Evaporation	
PLANT SIZE: Feed = 45,000 lbs/hr 2 1/2% sulfuric acid waste water		PLANT SIZE: Feed = 45,000 lbs/hr 2 1/2% sulfuric acid waste water	
CAPITAL COSTS: Assumes zero capital investment cost. Existing lime precipitation system requires no capital improvements.		CAPITAL COSTS: \$2,925,000 (316 ss construction)	
ANNUAL OPERATING COSTS @ 330 days/yr operation		ANNUAL OPERATING COSTS @ 330 days/yr operation	
Chemicals		Chemicals	
Utilities @ \$0.033/kw-hr	\$114,000	Utilities @ \$0.033/kw-hr	\$0
Gypsum Disposal @ \$654/day	\$8,250	Gypsum Disposal @ \$654/day	\$233,860
Maintenance @ \$137/day	\$216,000	Maintenance @ 6% of capital investment per year	\$0
Operating Labor (incl. overhead & fringes) @ \$873/day	\$50,000	Operating Labor (incl. overhead & fringes) @ \$436/day	\$175,500
	\$319,000	Sulfuric acid credit @ \$50 /ton	\$160,000
			(\$311,700)
TOTAL ANNUAL COST	\$707,250	TOTAL ANNUAL COST	\$257,660

Source: Arthur D. Little, Inc.

Radford AAP, 3.3¢/kw-hr, we see that the operating cost of the MVR evaporation system is \$450,000/yr lower than that for the standard lime precipitation process, (\$257,000 vs \$707,000/yr) giving 6½ year pay out on the \$2.92 MM investment.

Table 3-5 uses the U.S. Army's system of Present Value Analysis to take into account both capital and operating cost for comparing the two processes (Ref 52). Here we have assumed that the lime neutralization process requires no capital improvements and the MVR evaporation process is built over a one year period (time 0 to end of year 1). Further, both processes are assumed to have a ten-year operating life beginning the moment the MVR evaporation system is completed, and neither has a salvage value.

Again, using electricity at 3.3¢/kw-hr, and the recommended 10% per year discount rate, we see that the MVR evaporation system will just barely not pay for itself in the 10 year period (net present value = -\$0.16MM, or a present value of saving to investment ratio of only 0.944). A "profitable" venture would have a ratio greater than 1.0; the 1.0 in effect is a 10% discounted cash flow (DCF) rate of return.

We performed a sensitivity analyses of the effect of electricity cost and sulfuric acid byproduct value on the economic viability of the MVR evaporation system compared to the lime precipitation process, Figure 3-5. We see that to achieve a Savings (over the lime precipitation process) to Investment ratio of 1.0 with \$50/ton sulfuric acid credit requires an electricity cost of no more than 2.9¢/kw-hr. We show effect of electricity cost from 6.0¢/kw-hr to 2.0¢/kw-hr to encompass the likely range among the AAPs (Sunflower has 5.5¢/kw-hr electricity cost; a plant with excess high pressure steam could use a steam turbine in place of electric motors thereby achieving equivalent electricity cost in the 2¢/kw-hr range). Also the effect on profitability of sulfuric acid credit as high as \$70/ton was included in the sensitivity chart of Figure 3-5 as there are projections of sharply increasing sulfur prices in the 1990's as a result of a shortage of "Frasch" sulfur.

In any case, under present economic conditions, the presence of inexpensive electricity, or availability of excess high-pressure steam (for turbine-driven compressors) are necessary to make the MVR evaporation process attractive.

Perhaps an even more important factor is that the above calculations are based on full capacity operation (330 days/yr). At lower rates of utilization, this process and all the others considered herein, because of their capital intensity, would be economically less attractive than the "sunk cost" lime precipitation process.

Figure 3-6 shows the effect of operation rate on annual operating cost for the six more promising processes. The cost elements for these plots are from Tables 3-3 and 3-4 modified to include labor for each process, two persons/shift except one/shift for Process 6. Also, electricity was

TABLE 3-5

ECONOMIC ANALYSIS: MECHANICAL VAPOR RECOMPRESSION EVAPORATION  
VS EXISTING LIME PRECIPITATION SYSTEM

1. Title: COMPARATIVE ECONOMIC ANALYSIS OF SULFURIC ACID WASTEWATER TREATMENT METHODS
2. Objective: TO COMPARE PROPOSED MECHANICAL VAPOR RECOMPRESSION EVAPORATION WITH EXISTING LIME PRECIPITATION SYSTEM
3. Present Alternative: EXISTING LIME PRECIPITATION SYSTEM  
3a. Economic Life: 11 years
4. Proposed Alternative: MECHANICAL VAPOR RECOMPRESSION EVAPORATION  
4a. Economic Life: 11 years
5. Discount rate: 10.00%

Project Year	Mid-Year Discount Factors	Proposed Alternative			Existing Alternative			Discounted Annual Costs		Present Value of Savings
		Investment Costs	Operating Costs	Total Annual Costs	Investment Costs	Operating Costs	Total Annual Costs	Proposed System	Existing System	
1.00	0.955	\$2,925,000	\$0	\$2,925,000	\$0	\$0	\$0	\$2,792,045	\$0	(\$2,792,045)
2.00	0.868	\$0	\$257,660	\$257,660	\$0	\$707,250	\$707,250	\$223,589	\$613,729	\$390,140
3.00	0.789	\$0	\$257,660	\$257,660	\$0	\$707,250	\$707,250	\$203,263	\$557,936	\$354,673
4.00	0.717	\$0	\$257,660	\$257,660	\$0	\$707,250	\$707,250	\$184,785	\$507,214	\$322,430
5.00	0.652	\$0	\$257,660	\$257,660	\$0	\$707,250	\$707,250	\$167,986	\$461,104	\$293,118
6.00	0.593	\$0	\$257,660	\$257,660	\$0	\$707,250	\$707,250	\$152,714	\$419,185	\$266,471
7.00	0.539	\$0	\$257,660	\$257,660	\$0	\$707,250	\$707,250	\$138,831	\$381,078	\$242,246
8.00	0.490	\$0	\$257,660	\$257,660	\$0	\$707,250	\$707,250	\$126,210	\$346,434	\$220,224
9.00	0.445	\$0	\$257,660	\$257,660	\$0	\$707,250	\$707,250	\$114,737	\$314,940	\$200,204
10.00	0.405	\$0	\$257,660	\$257,660	\$0	\$707,250	\$707,250	\$104,306	\$286,309	\$182,003
11.00	0.368	\$0	\$257,660	\$257,660	\$0	\$707,250	\$707,250	\$94,824	\$260,281	\$165,457
TOTALS		\$2,925,000	\$2,576,600	\$5,501,600	\$0	\$7,072,500	\$7,072,500	\$4,303,291	\$4,148,211	(\$155,079)

TOTAL PRESENT VALUE OF SAVINGS INCLUDING CAPITAL INVESTMENT:

(\$155,079)

TOTAL PRESENT VALUE OF PROPOSED CAPITAL INVESTMENT:

\$2,792,045

TOTAL PRESENT VALUE OF SAVINGS EXCLUDING CAPITAL INVESTMENT:

\$2,636,966

SAVINGS (EXCLUDING CAPITAL INVESTMENT)-TO-INVESTMENT RATIO:

0.944

Source: Arthur D. Little, Inc.

# Effect of Power Cost on Profitability

MVR Evaporation vs Lime Precipitation

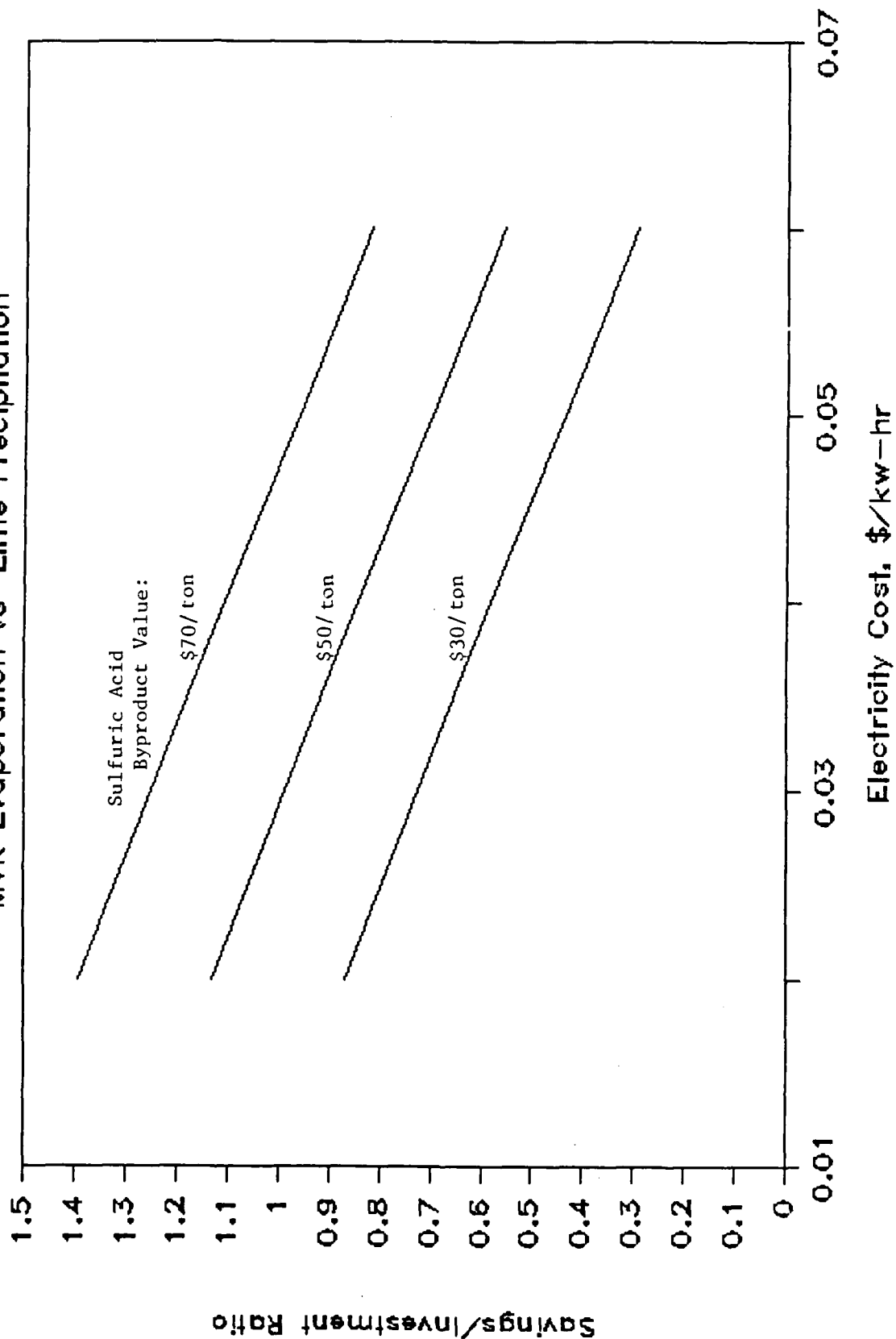


FIGURE 3-5

Source: Arthur D. Little, Inc.

# OPERATING RATE VS ANNUAL COST

(BASIS: RADFORD'S SAR DESIGN RATES)

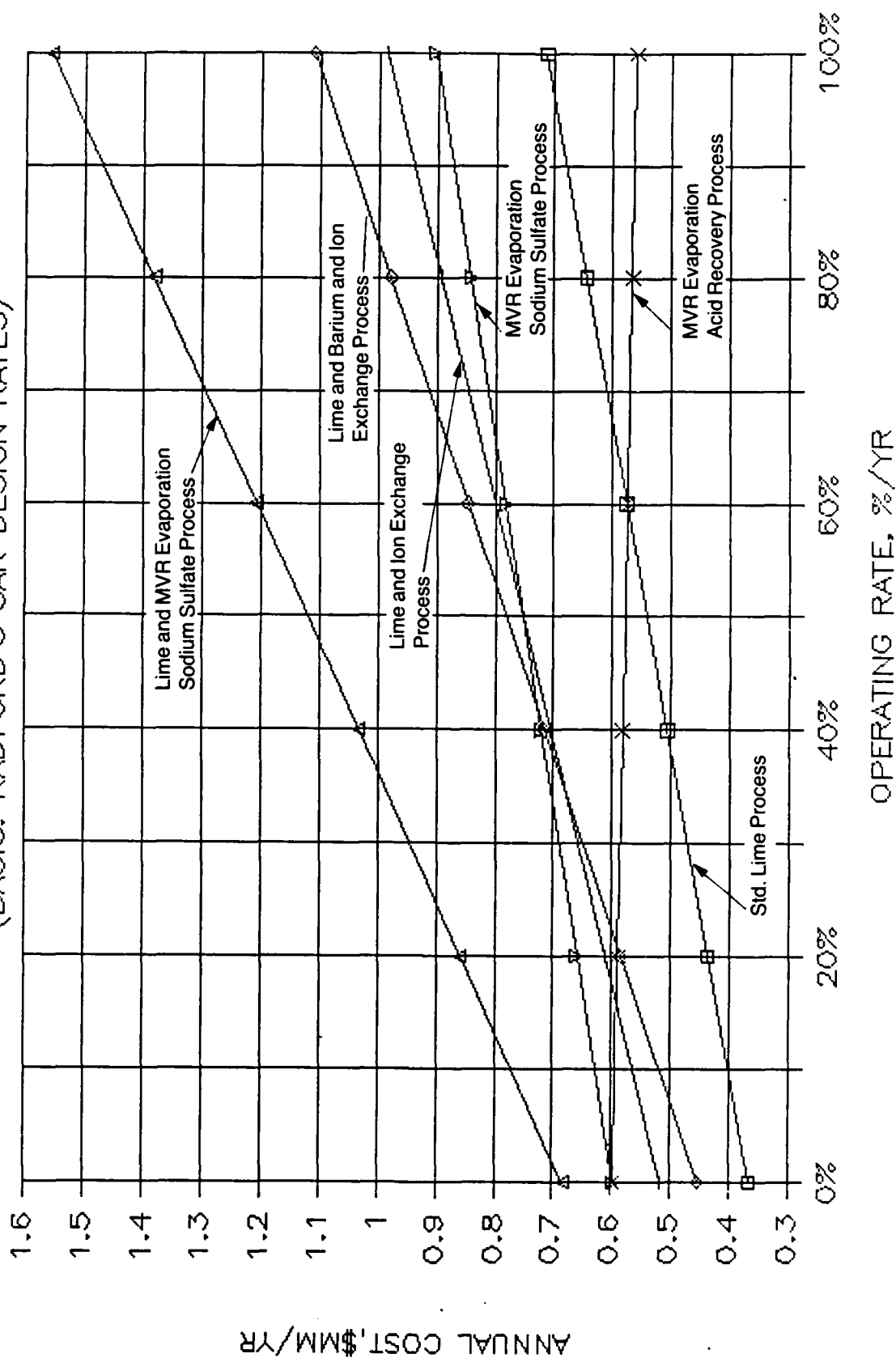


FIGURE 3-6

Source: Arthur D. Little, Inc.

taken at 5¢/kw-hr to reflect a national average rather than the special Radford AAP situation.

A study of Figure 3-6 shows that at low operating rates, the lime precipitation process has the least annual cost (fixed plus variable cost). Further, it is the least expensive at all operating rates - up to 100% - except for the MVR evaporation process which, because of the byproduct sulfuric credit, becomes more attractive above the 60% operating rate.

Thus, only in wartime conditions of high operating rates would the MVR evaporation process make economic sense. Also it should be pointed out there is, to our knowledge, no operating experience using MVR evaporation to concentrate dilute solutions of sulfuric acid. One power plant, (Public Service of New Mexico, Four Corners, NM) however, uses these same mechanical compressors to compress a wet  $\text{SO}_2$  gas stream (i.e., somewhat comparable corrosion service) and report good service life using tantalum compressor blades. (Radford AAP engineers point out that 33%  $\text{H}_2\text{SO}_4$  is more corrosive than wet  $\text{SO}_2$ , so that the adequacy of tantalum compressor blades is a key issue to this process.)

### 3.5 Conclusions

In our ranking system, the MVR evaporation system scored the highest of the eight processes considered, a score of 20 out of possibly 30, with the second highest ranking process having a score of only 14, and the standard lime precipitation process scoring only 13 (Table 3). Further, of seven judgmental categories considered, the MVR evaporation process ranked highest of all processes in three of these categories, second highest in one. It ranked lowest in two categories, which included perceived annualized cost (a zero rating along with four other proposed processes).

Yet a preliminary cost analysis showed the MVR evaporation process to have the lowest operating cost of any process considered, lower even than the standard lime precipitation process (Table 3-3); this was further confirmed in a more detailed comparison with the lime precipitation process, (Table 3-4). Only when new capital investment is taken into account along with low operating rates (and one considers the investment in the lime precipitation process as a sunk cost) does the MVR evaporation process become uneconomic. Even at reasonably low electric rates the savings in operating cost are just not enough to pay for the capital investment over the ten-year life allowed for the venture.

In view of this economic hurdle and the potential corrosion hurdles, it bears repeating the virtues of the MVR evaporation system:

- It requires less space than any other process; the evaporator and compressor could be located within or directly adjacent to the SAR unit.

- If located next to an SAR unit, only incremental labor would be required (less than 1 person).
- The recovered sulfuric acid would be recycled directly to the process; no marketing of byproducts required.
- There would be no solids handling problem.
- If effective mist eliminators are used, the evaporator condensate should be reusable in the process; i.e., zero discharge would be achievable.
- The poor economics of this process are due in part to the assumption of no capital investment being required for the lime process, when in fact significant revisions may be required to meet several states' environmental standards.

To our knowledge, MVR evaporation has never been used for sulfuric acid recovery; at the 24% concentration level and today's energy and sulfur prices it would not be economic to recover it. Looking to the future, with rising sulfur prices and zero discharge more the rule than the exception, it is conceivable the U.S. Army may view piloting such a new recycle process. If the corrosion rate of the proposed tantalum compressor blades is not an insurmountable problem, the piloting of such a system could contribute to improving the state of the art in acid recovery, both for the sake of the AAPs and the sulfuric acid industry in general.



## SECTION 4

### POSSIBLE TEST PROGRAM FOR IMPROVEMENTS TO THE LIME PRECIPITATION PROCESS

#### 4.1 Why the Lime Precipitation Process?

The lime precipitation process for treating dilute sulfuric acid wastes has the following reasons for selecting it for further improvement:

- It is as advanced as any sulfuric acid neutralization process used in industry;
- It removes 90-95% of the sulfate as insoluble, innocuous calcium sulfate; and
- It is the primary waste treatment process installed in all of the AAPs.

But at the one active site, Radford AAP:

- It is plagued with excessive downtime and maintenance due primarily to severe scaling of equipment;
- It experiences poor turbidity control due to excessive fines from the precipitation; and
- It experiences wide excursions in pH, exceeding state environmental limits.<sup>(1)</sup>

Furthermore, at AAPs in some other states, there was concern in the past for the high soluble sulfate in the treated effluent from the lime precipitation process, thus fostering secondary treatment to remove this soluble sulfate. However, the secondary treatment subsequently installed in two of these AAPs, ion exchange and barium precipitation with ion exchange, is totally dependent on good control (particularly elimination of fines) by the upstream lime precipitation process. These processes have never operated commercially; the Radford experience would suggest they will experience extreme difficulty because of the deficiencies in the lime treatment operation.

#### 4.2 Inherent and Design Deficiencies of the Lime Precipitation Process

Some inherent deficiencies in any lime precipitation process are:

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<sup>(1)</sup> This waste is combined with another waste stream prior to discharge and the combined stream meets the state environmental limits.

- The very low solubility of lime (it is less than that of the precipitated  $\text{CaSO}_4$ ) and goes into solution only because any sulfuric acid present reacts with the dissolved lime, thus continually shifting the equilibrium.
- The slowness of the lime/sulfuric acid reaction - it is dependent on the rate of solution of the lime particles which, in turn, depends on the particle size of the ground lime. Depending on particle size, the reaction takes 5 to 15 minutes (Ref 37).
- The steepness of the pH vs acidity curve for the lime/sulfuric acid reaction, leading to an overshooting of the lime addition due to false (or rather transient) acid pH readings.
- The propensity for the resultant  $\text{CaSO}_4$  precipitate to precipitate out on (i.e., coat) the still dissolving lime particles.

These inherent limitations of the chemistry of the neutralization are probably exacerbated by:

- The low residence time provided for in the design of the process. For example, at Radford AAP the residence time in the neutralizer is only 8 minutes, and sometimes at actual flow rates, the residence time is less than 4 minutes. This in itself would lead to excessive fines.
- Poor mixing and poor pH control, the latter itself due in part to poor mixing, as well as slowness of the reaction and other factors discussed below.

#### 4.3 Objectives and Rationale for Improving the Process

Thus, the objectives or goals for improving the operability of the process would be:

- (1) to reduce mechanical disruptions (due to scale formation);
- (2) to reduce turbidity problems in
  - clarifier overflow to river;
  - filtrate (which now must be recycled);
- (3) to reduce soluble sulfate in effluent.

This would be done by means of improved pH control, seed recycle and internal liquor recycles; more precisely:

- Better pH control should:
  - reduce the incidence of excess lime usage;
  - reduce the incidence of pH excursions; and
  - encourage better crystal growth.
- Calcium sulfate seed recycle should result in:
  - larger crystals;

- reduced fines; and
  - reduced scaling of equipment.
- Reuse of filtrate and clarified water for lime slaking and filter washing, respectively, would result in a:
    - reduction in fresh water usage;
    - reduction in soluble sulfate to the river; and
    - reduction in water load to the clarifier.

#### 4.4 Seed Recycle

Crystallization processes often use seed recycle as a means of growing bigger crystals and, therefore, reducing fines by virtue of minimizing incipient nucleation. This seed recycle can be accomplished internally within the crystallizer ("Oslo" Classifier, for example) or externally (sugar crystallization, for example).

The same principles of crystal growth apply to chemical precipitations as apply to crystallization processes. In chemical precipitations, the driving force is the exceeding of solubility by increasing concentration via creating new product; in crystallization, the driving force is by increasing concentration via evaporation of water (sugar crystallization) or by reducing solubility via lowering temperature (Oslo Classifier).

In 1969, Judkins & Parsons published an investigation of chemical precipitation of  $\text{CaSO}_4$  on to seed crystals of the same material (Ref 28). They found that the resultant larger crystals settled faster, gave a better (reduced) sludge volume index and lower specific resistance (in filtration). Optimum conditions for neutralizing synthetic  $\text{H}_2\text{SO}_4$  waste, actual plating waste and viscose rayon wastes were at seed recycle ratios of roughly 3:1 to 5:1 recycle seed to incipient new seed.

In checking with the Dorr Oliver Company (manufacturer of filters and clarifier/thickeners) they indicated good experience with seed recycle, especially at even higher recycle ratios, up to 10:1, and indicated that Bethlehem Steel Company had developed a proprietary process, available for licensing, for neutralizing sulfuric acid pickling liquors that used as high as a 40:1 seed recycle ratio (we did not talk directly with Bethlehem Steel on their process). The Dorr Oliver engineers indicated that high seed recycle gave not only better crystal formation, but because of the vastly increased surface area available in the neutralizer at the time of incipient crystallization of newly formed  $\text{CaSO}_4$ , less (percentage wise) would precipitate onto the equipment or onto the undissolved lime particles.

A logical question is, can we achieve such high recycle rates of  $\text{CaSO}_4$  seed, given that the current precipitate has difficulty settling. This is a "chicken and egg" situation. We need settled crystals to recirculate to give bigger crystals that will settle faster. One way is to start up the lime precipitation process at a slow rate, both to give more residence time in the neutralization (for crystal growth) and lower

effluent upflow rates in the clarifier/thickener. (The crystals must settle in the opposite direction to this upflow velocity.)

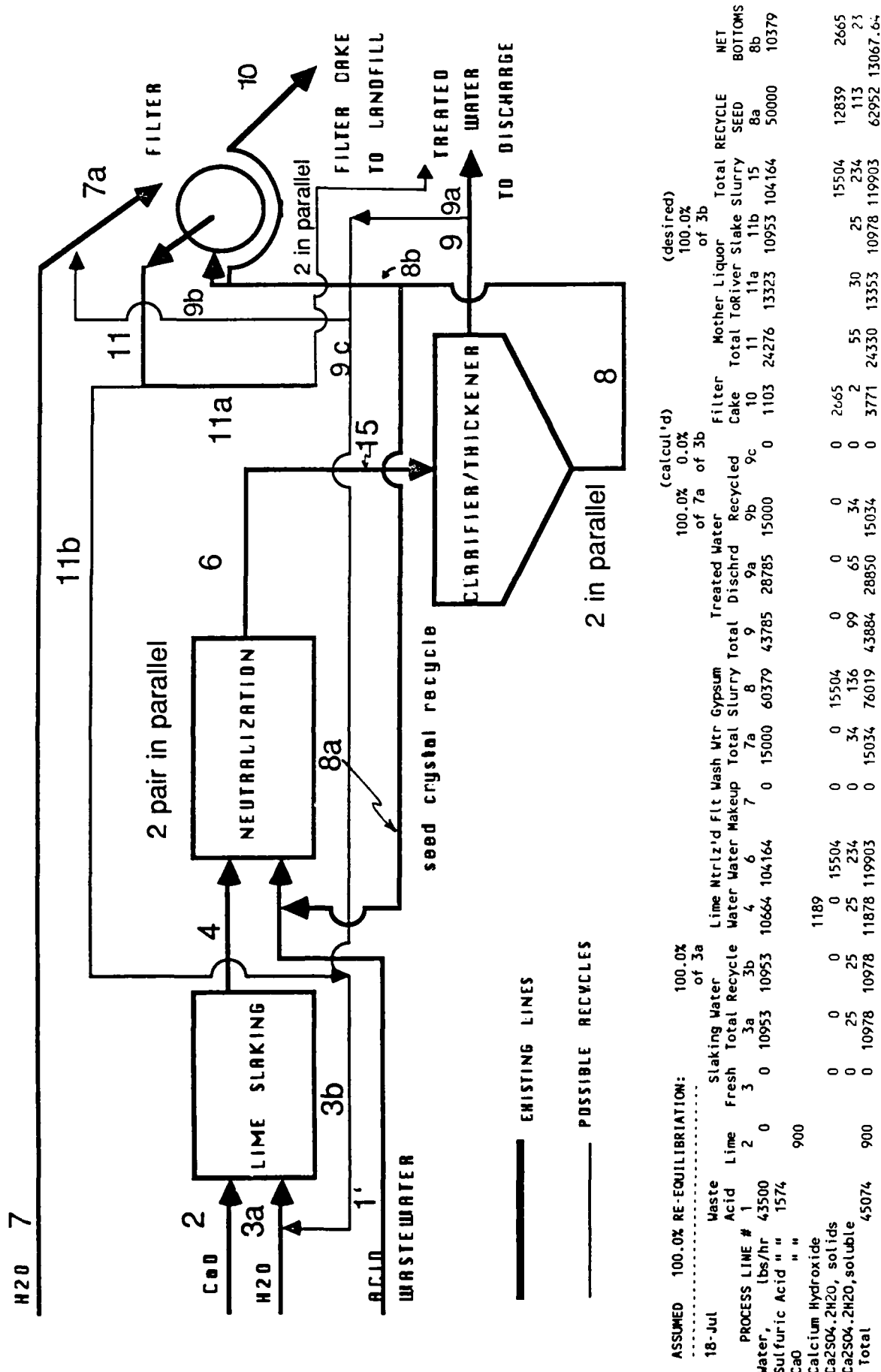
The clarifier/thickener at Radford AAP appears to be appropriately sized for settling out any reasonable size crystals, i.e., 400 mesh or bigger. For example, the "rule of thumb" for designing settlers for minerals is 1 gal/min per ft<sup>2</sup>. The Radford AAP thickener was designed for only 0.217 gal/min per ft<sup>2</sup>. The fact that Radford AAP reports carryover of turbidity from the clarifier indicates very fine crystals indeed. For example, if we assume turbidity carryover only occurs at the fastest upflow rates reported at Radford, i.e., 0.45 gal/min per ft<sup>2</sup>, then from Stokes law we calculate the overflowing crystals are .02 mm diameter or finer, i.e., approximately 800 mesh.

Figure 4-1 shows a flow diagram of the lime precipitation process with incorporation of a CaSO<sub>4</sub> seed recycle to the neutralization. (The "1-2-3" spread sheet of Section 2.1.1 was modified to divide the thickened CaSO<sub>4</sub> stream, No. 8, into two parts, part for recycle, the net to the filtration.) It should also be noted that the filtrate from the rotary vacuum filter is assumed to be turbidity free, so that it can be discharged directly to the river with a portion of this filtrate used as water for the lime slaking operation. Thus, to the extent that solids are taken off the bottom of the clarifier (to go to the filter, thence the river), the less clarifier upflow, gal/min per ft<sup>2</sup>, required (i.e., discharge to the river via the clarifier overflow). This increases the ability of the clarifier/thickener to settle solids and, as solids are recirculated through the system, this increases the solids content fed to the thickener which again tends to improve settling. Figure 4-2 is a plot of the effect of thickener upflow rate on the percent of the treated clarified liquor that must be clarified, by the filter, vs that which passes as clarified effluent from the clarifier/thickener. It also shows the increase in solids concentration as a result of the above mentioned phenomena. At 0.155 gal/min per ft<sup>2</sup> upflow rate, all of the water load that must be discharged to the river can be handled by the clarifier. This compares with the design rate of 0.217 gal/min per ft<sup>2</sup>. This higher upflow rate in the original design was a result of dilution by use of fresh water in the system.

Figure 4-3 is a plot showing the relationship between thickener upflow rate and seed recycle rates to achieve various seed-to-new-sulfate ratios; the assumption being that the upflow rates are sufficiently low enough so as to still be able to obtain a clear effluent. It can be seen that at the Radford AAP design waste flow input and concentration, to achieve a 5:1 seed recycle requires a 50,000 lb/hr seed recycle rate coupled with only a 0.14 gal/min per ft<sup>2</sup> thickener upflow rate. This upflow rate corresponds to the settling of all crystals down to only 11 microns. Thus it appears that the thickener should be capable of recycling sufficient calcium sulfate seed to achieve adequately high seed recycle ratios. The material balance shown at the bottom of Figure 4-3 is for the flow conditions cited above (5:1 seed recycle at a 50,000 lb/hr seed recycle rate).

FIGURE 4-1

# LIME PRECIPITATION SYSTEM WITH SEED RECYCLE



Source: Arthur D. Little, Inc.

# EFFECTS OF UPFLOW RATE

(BOTTOMS RECIRCULATION @ 50000 LBS/HR)

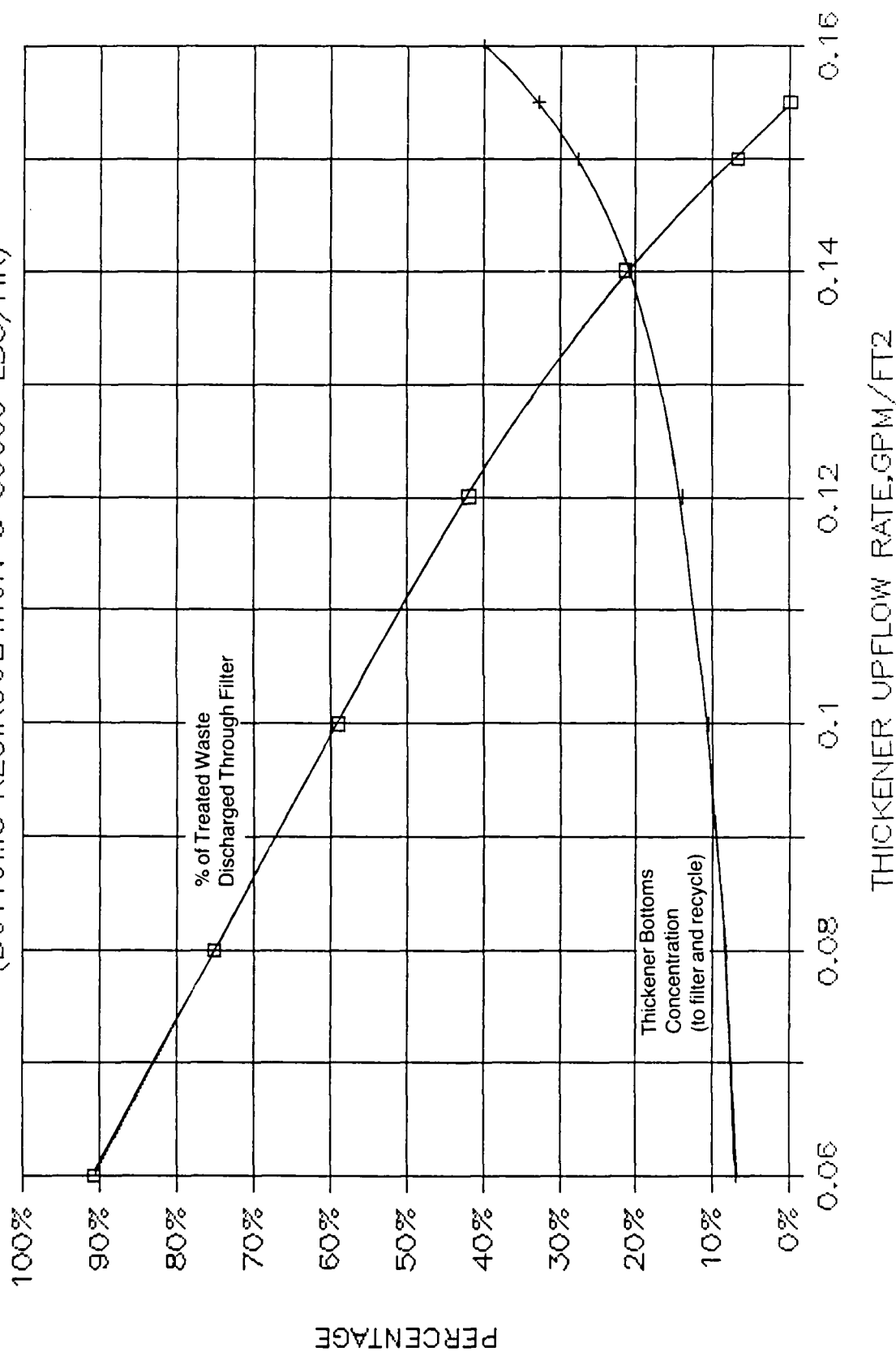


FIGURE 4-2

Source: Arthur D. Little, Inc.

# SETTLING & RECYCLE RATES VS SEED RATIO

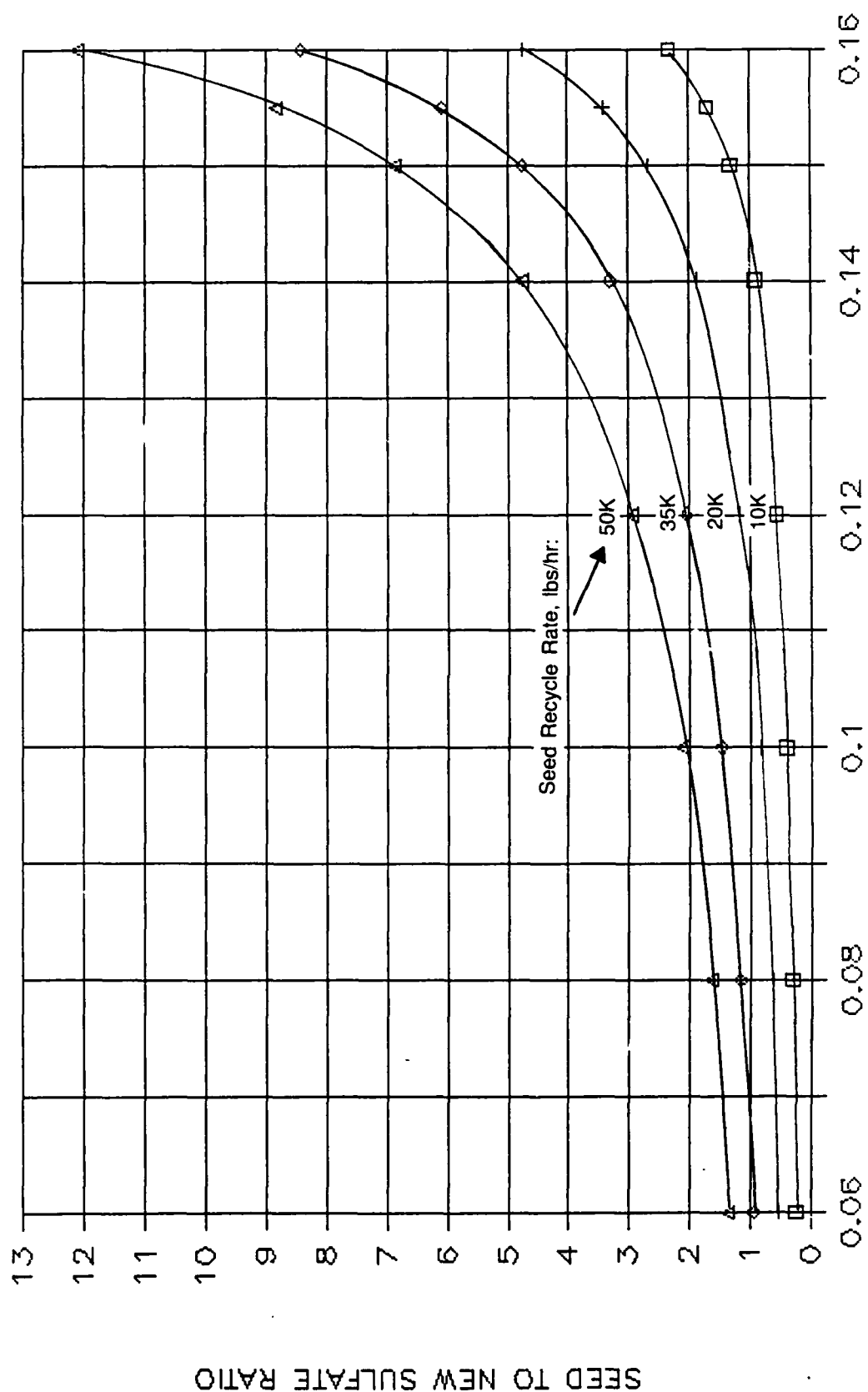


FIGURE 4-3

Source: Arthur D. Little, Inc.

#### 4.5 Overall Approach

All of our discussions have been with the Radford AAP system as designed. Very recently they have modified the process to that shown in Figure 4-4, using a minimum of piping changes as indicated by the arrows. However, the consequence is very profound as shown by the net schematic, Figure 4-5. (This is to be compared with the design-standard process Figure 2-1.) One clarifier is used as a hold-up tank, all of the liquor passes through the filter, and the filtrate, typically turbid, is sent to the second clarifier (now at twice the upflow rate per ft<sup>2</sup> of surface), thence to the river.

Since this system has never been tested, we would first document the performance of the existing system, thence the original design-basis system, and finally the proposed system with seed recycle, internal water recycle and better pH control, etc.

We would evaluate the existing and originally designed system via:

- Collection of grab samples for laboratory analysis, pH vs. time in:
  1. 1st neutralizer tank
  2. 2nd neutralizer tank
- Regression analysis to sort out the magnitude of the effects (independent) variables and which of these are "best" for production and which for control of the process. Thus:

$$Y = f(X_1, X_2 \dots X_N) \text{ where}$$

the dependent variables would be:

Y = ultimate pH (lab test which because of delays in sampling and analysis takes into account the effect of time for the already-added lime to go into solution.

and

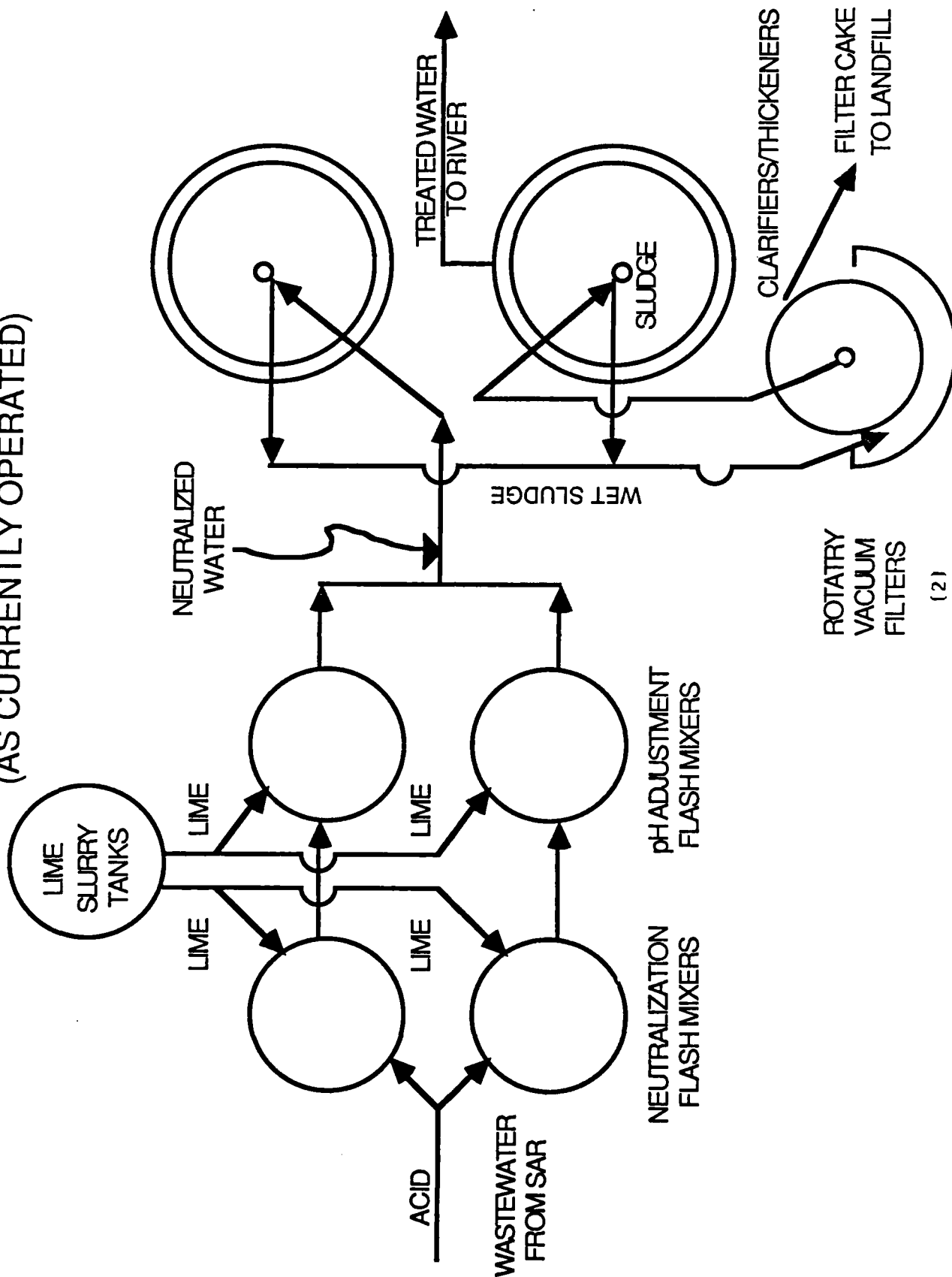
Y = real time pH (line meter in the process) which per force measures the solution pH without taking into account the undissolved lime.

The independent variables would be evaluated in the above regression equations both to see which variables are best for production of ultimate pH and which are best on control of the neutralization process. These include:

- initial acid wastewater acidity;
- initial acid wastewater conductivity;
- lime concentration (acid equivalent);
- lime reactivity;
- lime flow rate (1st and 2nd neutralizers);
- line meter pH (1st and 2nd neutralizers);



# RADFORD AAP LIME PRECIPITATION SYSTEM (AS CURRENTLY OPERATED)



(2)

FIGURE 4-4

Source: Arthur D. Little, Inc.

# **RAO FORD AAP LIME PRECIPITATION SYSTEM** **(AS CURRENTLY OPERATED)**

H<sub>2</sub>O

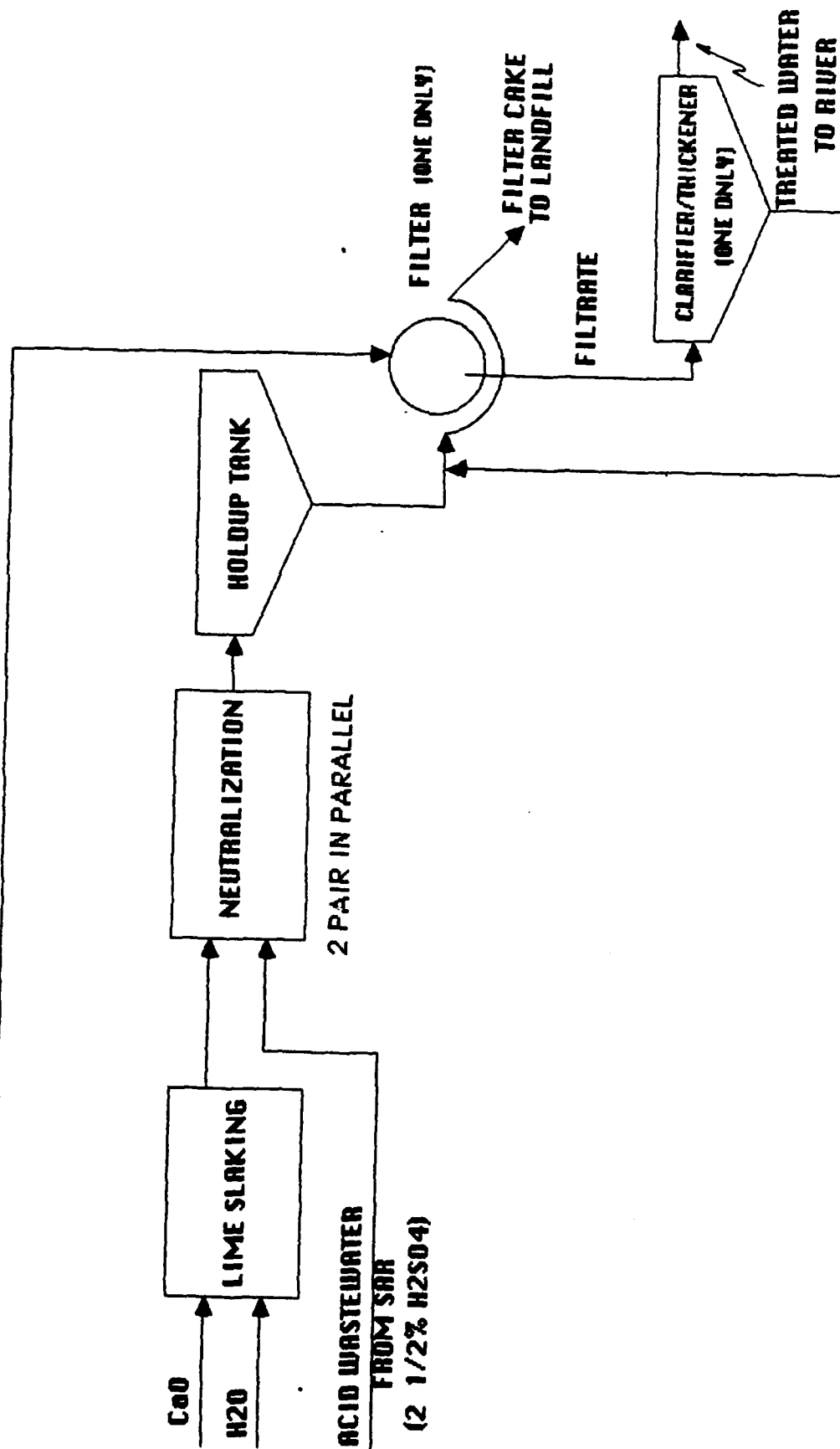


FIGURE 4-5

Source: Arthur D. Little, Inc.

- residence time (1st and 2nd neutralizers);
- total residence time; and
- change in lab-measured pH with time (1st and 2nd neutralizers).

We would then evaluate new pH control systems, for example:

- Test the use of conductivity of incoming acid wastewater for feed forward control of lime addition to 1st neutralizer.
- Test the use of pH of 2nd neutralizer for feed-back control of lime addition to this neutralizer, but with the pH set point adjusted by the pH of the final effluent.

Finally, we would evaluate means of improving crystal size and reducing scaling via the proposed process change, i.e.:

- Test recirculation of calcium sulfate seed;
- Test in-line Kenics mixers;
- Test low rpm mixer impellers in the neutralization tanks; and
- Hang "scaling test plates" in 1st and 2nd neutralizers to quantify scale buildup per unit time (this same procedure would be used to test scale buildup at standard conditions, i.e., at the original design condition of #1 above).

#### 4.5.1 Sequence of Testing Before Production Campaign:

- Install piping and pump for sulfate seed recycle;
- Install extra pH probes as indicated; and
- Install piping to permit reverting to original design conditions.

#### Testing Sequence:

- Performance of existing piping modification (clarifier/thickener as Holdup Tank in series):
  - minimum 3 days test.
- Performance of standard plant layout:
  - with advanced pH control but varying production rate: minimum 3 day test; and
  - with advanced pH control but constant design feed flow rate and concentration of acid wastewater: minimum 3 day test.

- Recycle of seed with Kenics in-line mixers:
  - with advanced pH control but with constant design feed flow rate and concentration, evaluate 15,000, 35,000, 50,000 lb/hr recycle: minimum 3 day test; and
  - above test but normal variation in production rate and concentration: minimum 3 day test, maximum test period to duration of production campaign.

#### 4.5.2 Some Testing Details by Unit Operation

Two generic problems should be addressed in this test series:

1) significant variations in flow rate and acid concentration to the lime precipitation plant, and 2) not being able to handle "too dilute acid." An approach would be:

1. Let flow rate and acid concentration vary normally; use statistical analysis to see if variation adversely effects control of the lime precipitation waste treatment process.
2. Test keeping flow rate to lime precipitation process constant by sending excess acid wastewater to other waste treatment systems.

With respect to acid concentration, the test plan might be as follows:

Test constant acid wastewater feed:

- high acid concentration (say 2½%)
- low acid concentration (say ½%)

using 1) bucking-up with concentrated acid; or 2) dilution with water, as necessary.

A portion of the program on better pH control might include:

- 1) Lab test of conductivity vs. acidity mg/ml.
- 2) During normal (varying) feed conditions, test use of conductivity for feed forward control of acid addition vs. pH as feed back control.
- 3) Agitate feed hold up tank. Test on/off effectiveness of agitation by: std. dev. (conductivity, in) vs. std. dev. (conductivity, out). Test for significant improvement using the statistical "F" test;

$$F = \frac{\overline{\sigma}_{in}^2}{\overline{\sigma}_{out}^2}$$

With respect to the lime slaking operation, we would propose the following:

- 1) Alter piping to permit use of filtrate from rotary vacuum filter for lime slaking. From literature references the following is anticipated:
  - a slight increase in slaking time (slightly);
  - reduction in fresh water consumption by approximately 16%;
  - reduction in clarifier/thickener upflow rate by approximately 16%;
  - minimization of calcium carbonate scaling of the slaking equipment (carbonate from the fresh water); and
  - improvement in filtrability of the calcium sulfate filter cake.
- 2) During test runs check reactivity of the lime. Perform a statistical analysis of variations in lime reactivity vs. downstream pH control.

With respect to the clarifier/thickener, we would propose the following:

1) Process Modifications:

- a) Install piping and pump from thickener bottoms underflow back to neutralizer (3" pipe and approximately 5 HP pump for recycle rates to 100 gal/min);
- b) Install a pH meter on clarified overflow;
- c) Install flow measuring devices on:
  - bottoms flow to filter;
  - recycle line to neutralizer; and
  - overflow or feed to clarifier/thickener.

2) Testing:

- a) Obtain clarifier/thickener inlet grab samples:
  - sludge volume; and
  - initial pH, pH vs. time.
- b) Obtain clarified overflow grab sample:
  - suspended solids; and
  - initial pH.

c) Obtain bottoms grab sample:

- total solids; and
- initial pH, pH vs time.

d) Vary seed recycle rate (0, 15,000, 35,000, 50,000 lb/hr):

- 8 hours at each level of recycle;
- sample and test all of the above;
- note sludge volume in clarifier; and
- test effects of thickened solids on filtration as indicated in "Rotary Vacuum Filter Operation."

The rotary vacuum filter would require no process modifications, but we would propose to the extent instrumentation permits, note and test:

- pressure drop across filter (i.e., vacuum);
- flow rate;
- cake moisture;
- suspended solids in filtrate;
- dissolved solids in filtrate; and
- pH of filtrate.

## SECTION 5

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